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Dr. Lee A. DuBridge was consulting editor of the series from 1939 to 1946.

EXPERIMENTAL ATOMIC PHYSICS

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Pluris est oculatus testis unus quam auriti decem.
Qui audiunt, audita dicunt; qui vident, plane sciunt.

PLAUTUS.

PREFACE

The following introduction to the subject of experimental atomic physics is based upon a course that has been given to seniors and first-year graduate students during the past few years at Princeton University. The purpose of the course has been to present the subject from a predominantly experimental point of view. An endeavor has been made to incorporate in it certain of the simpler and more fundamental experiments, bearing most directly on the subject, that are suitable for performance by students. Out of the large number of possible experiments, those have been chosen which, in the opinion of the authors, demonstrate most clearly the basic physical principles and the concepts which are the foundation of the modern theoretical developments, or which measure in the most direct way the principal atomic constants. In the great majority of the experiments the necessary apparatus is already present in a physical laboratory or available commercially, or it may be constructed in a shop with only moderate facilities. Frequently, one or more alternative procedures are given, in order that the one best suited to the available apparatus may be chosen.

An attempt has been made to adopt a standard of technique that will yield results of sufficient accuracy to be significant, without involving the extreme labor necessary for the highest precision. In general, the experiments require the continued attention of the student for not more than a few hours, although the construction of the apparatus and its original assembly require considerable time. Just what fraction of this preliminary work can be done advantageously by the students themselves is a matter of opinion and depends to some extent on individual circumstances. One purpose of such an experimental course is to produce familiarity with instruments of research caliber and to engender in the student a proper respect for the attainment of the next decimal place.

Certain experiments, such as those concerned with Compton X-ray scattering, the Stern-Gerlach effect, and radioactive investigations requiring strong sources, are not described in detail because of the lengthy nature of the experiments or the difficulty of procuring the necessary materials. Subjects such as kinetic theory, specific heats, and gas discharges, which are also suitable for this type of presentation and for which many interesting experiments may be developed, have been omitted in order to keep the book within reasonable bounds. The apparatus in certain cases has been described in detail to facilitate its construction or to indicate dimensions that have been found satisfactory, but in general the details have been merely indicated, with as much flexibility as possible, and the apparatus may be constructed in accordance with available facilities. Many variations and improvements on the experiments that have been chosen will doubtless suggest themselves to the reader.

The aim has been to develop in as logical a manner as possible the theories of radiation and of matter, with particular attention to the fundamental conceptions and the experimental foundations upon which they are based. Partly for historical reasons and partly for purposes of presentation, the wave concept of radiation forms the starting point of the discussion. Certain of the experiments leading to the quantum or photon conception are then described and further evidence for the photon hypothesis is educed during the treatment of the quantized processes of interaction between radiation and matter. The structure of matter is considered in the reverse order. The fundamental experiments on atomicity and elementary masses and charges are the first to be introduced. The alternative wave or quantum-mechanical picture of matter is later discussed and the analogies between radiation and matter are there pointed out. The remaining chapters deal largely with the interaction of radiation and matter, proceeding from the electron phenomena of crystals, through the optical and X-ray ranges, to the subject of radioactivity and atomic nuclei.

The book has been designed as an introduction to atomic physics, and it is intended to follow a fairly solid grounding on the classical branches of the subject. It is presumed that the type of material included in a text on general physics has been covered thoroughly; in particular, a familiarity with the subjects of mechanics and electricity is essential. A working knowledge of calculus and elementary differential equations is also presupposed. Such theoretical material has been included as has been considered necessary for a systematic development, but it is hoped that the emphasis has remained predominantly on the essentially experimental nature of the subject. The mathematical treatments have been kept as simple as possible, and where results that cannot be obtained by direct and comparatively brief developments are required for the general argument, they simply have been stated and the appropriate reference given. Where alternative treatments are possible, the simpler one has been chosen.

Rather more references have been included than is customary in a textbook. This has been necessitated partly by the fact that a detailed theoretical development is precluded by lack of space (as well as possibly being inadvisable in a book of this nature), and partly because it is felt desirable for the student who intends to retain his interest in physics to become familiar with the literature and with the men who have developed the subject. An adequate discussion of the historical aspect of the various branches of atomic physics is, of course, not possible in a treatment of this length, and it is doubtful if any description brings out the scientific outlook of a period, or the experimental handicaps under which the foundations of the subject were laid, as forcibly as do the original papers. Furthermore the experimental difficulties, precautions, corrections, and incidental technique which have been found necessary for the attainment of extreme accuracy are nowhere so clearly shown as in the description by the investigators themselves. Finally, the modern lines of investigation, converging on the many fascinating problems of molecular, atomic, and nuclear structure, could at best be only indicated in the text, and for these the current periodicals provide the only adequate account.

We are particularly fortunate in having enjoyed the facilities of the Palmer Physical Laboratory for the development of the experiments that are described. We are greatly indebted to the members of the teaching staff, in particular to Professors E. U. Condon, H. P. Robertson, A. G. Shenstone, H. D. Smyth, and L. A. Turner, for their interest and assistance in the development of the course and for their suggestions and criticisms in the preparation of the manuscript. It is also a pleasure to acknowledge our indebtedness to Professor B. E. Warren of the Massachusetts Institute of Technology for certain suggestions in connection with the experimental work on X-rays. We are indebted to Mr. L. B. Rentschler and Mr. S. N. Van Voorhis for their assistance in the preparation of the photographs for reproduction.

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PALMER PHYSICAL LABORATORY,
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EXPERIMENTAL ATOMIC PHYSICS

CHAPTER I

THE VELOCITY OF PROPAGATION AND THE PRESSURE OF RADIATION

1-1. Introduction.—The branch of physics that has made possibly the greatest contribution to the development of modern physical concepts and theories is the study of radiant energy. The most familiar form of this is visible light, and it is hardly possible to overemphasize the extent to which our knowledge of physical phenomena depends on the discoveries that have been made in this field of investigation. The extent of visible radiation, or the range of the visible spectrum, is only a very small fraction of the complete radiant-energy spectrum. This extends over a vast range: radio waves, heat rays, visible and ultra-violet light, X-rays, γ rays emitted by radioactive substances, and possibly also cosmic rays. The knowledge gained from the investigation of visible light has formed the basis for our interpretation of the many diverse phenomena exhibited by the other forms of radiant energy. They are undoubtedly all of the same nature.

The unification of radiation phenomena, which exhibit many superficial differences, is due to Maxwell, whose theory of electromagnetic disturbances predicts the possibility of electromagnetic waves of any wave length but all traveling with the same velocity in empty space. The velocity of propagation of these waves is one of the most fundamental quantities in nature. Its importance may be seen from the fact that in any book on modern physical theory, c, which is universally used as the symbol for the velocity of light, appears upon almost every page. The value of this velocity is also predicted on the electromagnetic theory to be the same as the conversion factor by which electrostatic measurements may be changed into electromagnetic quantities, the so-called *ratio of the units*. This quantity, c, acquired a still greater importance with the advent of the theory of relativity; for upon this theory no energy may be transmitted with a velocity greater than that of light, and the square of this velocity represents the ratio between the energy of a body and its mass.

The theory that the phenomena of light are caused by material particles or corpuscles was so ably developed and expounded by Newton that it remained the prevailing scientific theory for approximately two hundred years. The demonstration that light travels faster in air than in water was a crucial experiment deciding unequivocally in favor of the electromagnetic theory as opposed to any theory identifying a light beam with a stream of material particles. There is also a great body of further evidence that all radiant energy may be considered to be electromagnetic in origin. Much of this evidence consists in the agreement between the predictions of the electromagnetic theory and the results of experiment in the field of optics. The phenomena of reflection, refraction, diffraction, polarization, dispersion, etc., are all very beautifully and completely accounted for on the theory of electromagnetic waves. All of these phenomena, however, lie outside the scope of this book, and in the following treatment we shall be concerned with only two experimental demonstrations. The first is that the velocity of light is equal to the ratio of the units, and the second is the verification of Maxwell's further prediction that light should exert upon any surface which it strikes normally a pressure equal numerically to the sum of the energy densities in the incident and reflected beams.

1-2. Electrical Units.—The *electrostatic* system of units is based on the definition of the unit electric charge. An electrostatic unit of charge is such that when it is placed 1 cm. from an exactly similar charge in a vacuum, the charges repel one another with a force of 1 dyne. From this definition the other units necessary to describe electrical phenomena may be derived. The *electromagnetic* system of units is based on the definition of the unit magnetic pole. This is a pole of such strength that when it is placed 1 cm. from an exactly similar pole in a vacuum they repel each other with a force of 1 dyne. From this definition all the other units necessary to describe magnetic phenomena may be obtained.

The fact that electricity and magnetism are interconnected enables magnetic quantities to be determined in terms of electrostatic units and electrical quantities in terms of electromagnetic units. Thus, while the electromagnetic unit of current is by definition that current which when flowing in a circle of 1-cm. radius exerts a force of 2π dynes on a unit magnetic pole at the center, this same current may be considered as due to the motion of some number of unit electrostatic charges flowing in the wire, *i.e.*, an electrostatic current. Experiment shows that this current is not one electrostatic unit of current, but it is a definite number, say c, of such units: *i.e.*, c electrostatic units (e.s.u.) of current equal one electromagnetic unit (e.m.u.) of current, so that c e.s.u. of charge equal 1 e.m.u. of charge, since a unit current in each system is a unit charge passing per second. Similarly, the electromagnetic unit of electric intensity is that electric field which exerts 1 dyne of force on 1 e.m.u of charge, *i.e.*, on c e.s.u. of charge. But c e.s.u. of charge are acted on by a force of c dynes in a unit electrostatic field, or by a force of 1 dyne in a field of $1/c$ e.s.u. Hence $1/c$ e.s.u. of electric field equals 1 e.m.u. of electric field. In an analogous manner it can be shown that all the electric and magnetic quantities may be expressed in either system of units by the use of a multiplying factor of c or c^2. This number c, called the *ratio of the units,* is experimentally found to have the value of about 3×10^{10}.

The capacity of a body is defined as the ratio of the charge on the body to its potential. So we may write

$$C_s = \frac{Q_s}{V_s} \quad \text{and} \quad C_m = \frac{Q_m}{V_m}$$

where C_s and C_m are the capacities, Q_s and Q_m the charges, and V_s and V_m the potentials in electrostatic and electromagnetic units respectively. Dividing one equation by the other we obtain

$$\frac{Q_s}{Q_m} = \frac{C_s V_s}{C_m V_m}$$

But the energy of the body, which is in ergs, must be the same in either set of units, so we have

$$\text{Energy} = \tfrac{1}{2}Q_s V_s = \tfrac{1}{2}Q_m V_m$$

or

$$\frac{V_s}{V_m} = \frac{Q_m}{Q_s}$$

If we substitute this ratio of the potentials in the preceding equation and remember that the ratio of Q_s to Q_m is c, we have

$$\frac{C_s}{C_m} = c^2 \quad \text{or} \quad c = \sqrt{\frac{C_s}{C_m}} \tag{1-1}$$

We thus see that the ratio of the capacity of a body in electrostatic units to its capacity in electromagnetic units is equal to the square of the ratio of the units of charge in the two systems.

There is a third system of units in use, known as the *practical* system. The absolute practical unit of current, the ampere, is defined as one-tenth of 1 e.m.u. of current. Similarly the absolute practical unit of potential, the volt, is defined as 10^8 e.m.u. of potential. Hence we have the following relations, which are frequently of use:

$$\begin{aligned} 1 \text{ ampere} &= 10^{-1} \text{ e.m.u. of current} \\ &= c \times 10^{-1} \cong 3 \times 10^9 \text{ e.s.u. of current} \\ 1 \text{ volt} &= 10^8 \text{ e.m.u. of potential} \\ &= \frac{10^8}{c} \cong \frac{1}{300} \text{ e.s.u. of potential} \end{aligned}$$

The *international* electrical units depend on experimental standards so chosen as to be as nearly as possible in agreement with the absolute units. The conversion factors for the current, potential and resistance between the two sets of units are:

1 international ampere = 0.99995 ± 0.00005 absolute ampere
1 international volt = 1.00046 ± 0.00005 absolute volts
1 international ohm = 1.00051 ± 0.00002 absolute ohms

Unless measurements are made to a very high order of accuracy, it is not necessary to distinguish between the absolute and international practical systems of units.

1-3. Maxwell's Displacement Current and Electromagnetic Waves.—Long before the time of Faraday and Maxwell it was known that whenever an electric field exists in a conducting material, there is a current of electricity, *i.e.*, a continuous motion of charges that lasts as long as the field is applied. Conductors apparently contain electric charges which are capable of more or less free motion through the substance under the influence of an electric field. On the other hand, insulators give no evidence of a steady electric current when a field is applied. It was known, however, that when a battery is connected across the terminals of a condenser an instantaneous current exists in the connecting wires. This charging current led Faraday to suggest that something analogous to a current exists in the insulator when the circuit is made.

In 1873, Maxwell effectively made the assumption that empty space and insulators contain elastically bound electric charges, capable of being displaced from their equilibrium position to an extent proportional to the strength of any applied electric field. When the field is applied, the charges move to their displaced positions and in so doing create a momentary *displacement current;* when the field is removed the charges return to their former positions, thus producing a momentary displacement current in the opposite direction. The displacement current exists, then, only when the field is changing.

As is shown in textbooks on electrical theory, there are two fundamental electromagnetic laws: (*a*) that the work to carry a unit magnetic pole once around a current of strength i e.m.u. is equal to $4\pi i$ ergs, and (*b*) that the induced e.m.f. around any circuit is equal to the rate of diminution of the magnetic induction through the circuit. When these laws are applied to a non-conducting region wherein the only current is the assumed displacement current, Maxwell's equations are obtained, which are as follows:

$$\frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z} = k\frac{\partial E_x}{\partial t} \tag{1-2}$$

$$\frac{\partial H_x}{\partial z} - \frac{\partial H_z}{\partial x} = k\frac{\partial E_y}{\partial t} \tag{1-3}$$

$$\frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y} = k\frac{\partial E_z}{\partial t} \tag{1-4}$$

$$\frac{\partial E_z}{\partial y} - \frac{\partial E_y}{\partial z} = -\mu\frac{\partial H_x}{\partial t} \tag{1-5}$$

$$\frac{\partial E_x}{\partial z} - \frac{\partial E_z}{\partial x} = -\mu\frac{\partial H_y}{\partial t} \tag{1-6}$$

$$\frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} = -\mu\frac{\partial H_z}{\partial t} \tag{1-7}$$

where H_x, H_y, H_z and E_x, E_y, E_z are the components of the magnetic and electric forces, respectively, while k and μ are the dielectric constant and the permeability of the medium, which are assumed to be constant over the region considered. All these quantities are taken consistently in either electrostatic or electromagnetic units. We have, in addition, the following expressions, if the medium contains no free charges or poles:

$$\frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z} = 0 \tag{1-8}$$

$$\frac{\partial H_x}{\partial x} + \frac{\partial H_y}{\partial y} + \frac{\partial H_z}{\partial z} = 0 \tag{1-9}$$

The Eqs. (1-2) to (1-7) describe the dependence of the time variation of the electric field upon the space variation of the magnetic field, and *vice versa*. To obtain an expression involving the derivatives of only one type of field, we may differentiate Eq. (1-2) with respect to t and from the result eliminate $\frac{\partial^2 H_z}{\partial y\,\partial t}$ and $\frac{\partial^2 H_y}{\partial z\,\partial t}$, found by differentiating Eq. (1-6) with respect to z and Eq. (1-7) with respect to y, giving

$$\frac{\partial^2 E_x}{\partial y^2} + \frac{\partial^2 E_x}{\partial z^2} - \frac{\partial^2 E_y}{\partial x\,\partial y} - \frac{\partial^2 E_z}{\partial x\,\partial z} = \mu k\frac{\partial^2 E_x}{\partial t^2}$$

If we both add and subtract the term $\partial^2 E_x/\partial x^2$, we obtain

$$\frac{\partial^2 E_x}{\partial x^2} + \frac{\partial^2 E_x}{\partial y^2} + \frac{\partial^2 E_x}{\partial z^2} - \frac{\partial}{\partial x}\left(\frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z}\right) = \mu k\frac{\partial^2 E_x}{\partial t^2}$$

But the quantity in parentheses equals zero by Eq. (1-8), so we have

$$\frac{\partial^2 E_x}{\partial x^2} + \frac{\partial^2 E_x}{\partial y^2} + \frac{\partial^2 E_x}{\partial z^2} = \mu k\frac{\partial^2 E_x}{\partial t^2} \tag{1-10}$$

Analogous partial differential equations may be found, by a similar procedure, for the other components of E and for the three components of H. Thus all the components of both the electric and magnetic fields obey the same partial differential equation, which is recognized as the so-called *wave equation*. That the solutions of this equation correspond to waves in the ordinary sense may be seen from a consideration of the simple case in which the disturbance, say ψ, is independent of

y and z, *i.e.*, it varies only in the x direction and with the time. In that case, we have

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{u^2}\frac{\partial^2 \psi}{\partial t^2} \tag{1-11}$$

where u^2 is written for $1/\mu k$. The general solution of this equation is $\psi = f_1(x - ut) + f_2(x + ut)$, where f_1 and f_2 are arbitrary functions (whose derivatives satisfy certain simple conditions), as may be verified by differentiation and substitution in Eq. (1-11). Consider the first term f_1. As $x + uT - u(t + T) = x - ut$, the value of the displacement due to this term at the distance $x + uT$ from the origin at the time $t + T$ is the same as the displacement at x at the time t. Hence this term represents a wave of arbitrary form progressing in the positive x direction with a velocity u. Similarly for the second term f_2, we have $x - uT + u(t + T) = x + ut$, so the displacement at a distance $x - uT$ from the origin at the time $t + T$ is the same as the displacement at x at the time t. Therefore this expression represents a wave advancing in the negative x direction with a velocity u.

Thus Maxwell's assumption of a displacement current, which produces the same magnetic effect as the familiar conduction current, predicts the possibility of electromagnetic waves traveling with a velocity $u = 1/(\mu k)^{\frac{1}{2}}$, where μ is the permeability and k is the dielectric constant of the medium. We have assumed that μ and k are both expressed in the same set of units, let us say electromagnetic units. By definition the force in dynes between two charges e_1' and e_2', r cm. apart in a medium of dielectric constant k', is $e_1'e_2'/k'r^2$, where the primes represent the expression of the quantities in electrostatic units. The force is, of course, the same if the quantities are expressed in electromagnetic units, *i.e.*, e_1e_2/kr^2. As 1 e.m.u. of charge equals c e.s.u., $e' = ce$, so the electrostatic-unit expression may be written $e_1e_2c^2/k'r^2$. Equating these last two expressions, we see that we must have: $k = k'/c^2$. By definition, the dielectric constant in electrostatic units for free space is unity and the permeability in electromagnetic units is unity, so $k\mu = 1/c^2$ or $u = c$. Therefore, the velocity of the electromagnetic waves predicted by Maxwell's theory is equal to the ratio of the units. If the experimentally measured velocity of light and the experimentally measured ratio of the units are found to be the same, this agreement constitutes strong evidence in favor of Maxwell's assumption of displacement currents and the electromagnetic nature of light. Further evidence for the theory comes from the measured velocity of electromagnetic waves on wires.

1-4. The Plane Simple Harmonic Electromagnetic Wave.—We shall consider electromagnetic waves which are emitted by a simple harmonic oscillator, *i.e.*, an oscillator in which the restoring force is proportional to the displacement. This oscillator, which must be composed of positive and negative charges with such a distribution that the simple harmonic relation is satisfied, we shall take as situated at the origin of coordinates. The variation with time of the electromagnetic wave must be given by the solution of the differential equation of such an oscillator, *i.e.*:

$$m\frac{d^2y}{dt^2} = -ay \tag{1-12}$$

The motion is considered to take place along the y coordinate, and a is the constant of proportionality between the restoring force and the displacement. A particular solution of this equation is a sine or cosine function of the time; choosing the cosine form we may write: $y = A \cos \omega' t$ where $\omega' = \sqrt{(a/m)}$; A is a constant of integration which represents the amplitude; the second constant of integration becomes zero by choosing $dy/dt = 0$ at $t = 0$. The wave emitted by this oscillator is spherical, analogous to the sound wave which would be emitted by a small vibrator in air. At a sufficiently great distance from such an oscillator, let us say along the x-axis, the radius of curvature of the wave is very large; to a first approximation we may take it as infinite, *i.e.*, the wave is approximately a plane wave. Hence the appropriate form of the function ψ representing such a simple harmonic plane wave is a cosine function of $\omega(x \pm ct)$ where ω has been written for ω'/c. Therefore we may write for the y component of the electric force, or the y displacement, at a great distance from the origin and at any time t:

$$E_y = A \cos \omega(x \pm ct) \tag{1-13}$$

From Eq. (1-3) or Eq. (1-7) we may write for the z component of magnetic force in free space:

$$H_z = \mp\frac{A}{c} \cos \omega(x \pm ct)$$

These functions are periodic in both x and t, and if we consider their variation with time at some point, let us say x, we can find the time T, known as the period, which is the least interval between identical configurations, *i.e.*:

$$\begin{aligned} \cos \omega(x + ct) &= \cos \omega[x + c(t + T)] \\ &= \cos \omega(x + ct) \cos \omega cT - \sin \omega(x + ct) \sin \omega cT \end{aligned}$$

For the two sides of this equation to be identical we must have:

$$\cos \omega cT = 1 \quad \text{and} \quad \sin \omega cT = 0$$

whence

$$\omega cT = 2\pi$$

In the time T, the wave, as pictured in Fig. 1-1, has moved a distance cT, which is the distance between identical displacements. This distance is the wave length λ. The reciprocal of this quantity, which is the number of waves per unit length, is known as the wave number $\tilde{\nu}$. The number of waves passing a given point per second, which is the frequency of the oscillator, or the reciprocal of T, is written as ν. Therefore we have the relations

$$\nu = \frac{1}{T} = \frac{c}{\lambda} = c\bar{\nu} = \frac{c\omega}{2\pi} \tag{1-14}$$

Thus ω may be eliminated from the equations for the electric and magnetic forces and these equations may be written in terms of T, ν, $\bar{\nu}$, or λ. Choosing the last we have:

$$E_y = A \cos \frac{2\pi}{\lambda}(x \pm ct) \tag{1-15}$$

$$H_z = \mp \frac{A}{c} \cos \frac{2\pi}{\lambda}(x \pm ct)$$

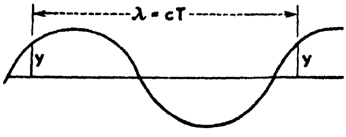

FIG. 1-1.—A simple harmonic wave.

These equations represent an infinite train of electromagnetic waves of wave length λ, polarized with the electric vector in the y direction and moving with a velocity c along the x-axis, in a negative or positive direction, depending on the sign chosen.

1-5. Experimental Evidence on the Value of the Ratio of the Units.—To determine the ratio of the electromagnetic to the electrostatic system of units, all that is required is to obtain an electrostatic and an electromagnetic measure of either charge, resistance, current, electromotive force, or capacity. A very accurate determination of this ratio was made by Rosa and Dorsey[1] in 1907. They employed a capacity method which they considered to be capable of much higher precision than any of the other methods which had been previously suggested or used. A simplified form of their procedure will be described later. They used spherical, cylindrical, and parallel-plate condensers, the second of these both with and without guard rings. Extraordinary care was taken to determine the dimensions of the condensers and to insure the proper alignment of their elements. The magnitude of the error which would be caused by a slightly improper alignment was calculated and corrected for, and corrections were also made for the inevitable mechanical deviations from a perfect electrical condenser. Great precautions were taken to eliminate errors due to the commutator which charged and discharged the condenser, *viz.*, the capacity of the commutator itself; the e.m.f. developed as it rotated in the earth's or any stray magnetic field; thermal and frictional e.m.fs. developed at its brushes; incompleteness of charge of the condenser if the brushes did not make long enough contact; variations in the speed of rotation; the action of the commutator as an electrostatic induction machine. The resistances used in the circuit were constantly checked to detect any variation in their value, and corrections were applied.

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[1] ROSA and DORSEY, *Bur. Standards Bull.*, **3**, 433 (1907).

The mean result of the work, which extended over three years, was:

$$c = (2.9971 \pm 0.0001) \times 10^{10} \text{ cm. sec.}^{-1}$$

when reduced to vacuum, and in terms of the international ohm. When this is corrected to the absolute ohm, the value becomes:[1]

$$c = (2.9979 \pm 0.0001) \times 10^{10} \text{ cm. sec.}^{-1}$$

The value of this ratio as determined by a number of the earlier investigators is given in the following table:[2]

Year	Investigators	Method	Ratio of units
1865	Weber and Kohlrausch[3]	Charge	3.1074×10^{10} cm. sec.$^{-1}$
1868	Maxwell[4]	E.m.f.	2.841
1889	Kelvin [5]	E.m.f.	3.004
1897	Fabry and Perot[6]	E.m.f.	2.9978
1907	Rosa and Dorsey[7,1]	Capacity	(2.9979 ± 0.0001)

The more recent of these determinations, as will be seen later, are in excellent agreement with Michelson's value for the velocity of light.

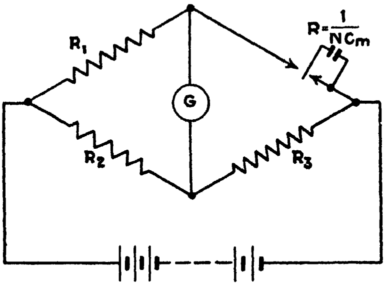

FIG. 1-2.—A bridge for measuring the ratio of the units.

1-6. Experiment to Measure the Ratio of the Units.—For the purpose of determining the ratio of the units with an accuracy of about 1 per cent, the following simple theory and apparatus are adequate. The capacity method is used, with a bridge and interrupter as shown in Fig. 1-2. If a condenser of capacity C_m, in electromagnetic units, is charged to a potential V_m, the charge on the condenser is $Q_m = V_m C_m$. If this condenser is charged and discharged N times per second, the total charge drawn from the source of potential per second is NV_mC_m. This may be considered to be equivalent to a steady current I_m, where $I_m = NV_mC_m$. But applying Ohm's law to such a circuit, we also have $I_m = V_m/R_m$

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[1] BIRGE, *Phys. Rev. Suppl.* (*Rev. Mod. Phys.*), **1**, 10 (1929).

[2] GLAZEBROOK, "Dictionary of Applied Physics," vol. II, p. 950 (1922).

[3] WEBER and KOHLRAUSCH, *Pogg. Ann.*, **99**, 10 (1856).

[4] MAXWELL, *Phil. Trans. Roy. Soc.* **158**, 651 (1868).

[5] GRAY, "Absolute Measurements in Electricity and Magnetism," Macmillan, p. 663 (1921).

[6] FABRY and PEROT, *Comptes rendus*, **124**, 182 (1897).

[7] ROSA and DORSEY, *Bur. Standards Bull.*, **3**, 433 (1907).

where R_m is the effective resistance, so that $1/R_m = NC_m$. Hence we may say that this condenser, charged and discharged N times per second, acts as if it were a resistance $1/NC_m$. If the condenser and switching device are put in one arm of a Wheatstone's bridge, the value of $1/NC_m$ may be found in terms of the other resistances in the network, and, if N is known, C_m may be calculated. When the bridge is balanced, either by varying N or the other resistances, we have the usual Wheatstone's-bridge relation

$$\frac{R_m}{R_3} = \frac{R_1}{R_2}$$

so that

$$C_m = \frac{R_2}{R_1 R_3 N} \tag{1-16}$$

Here the resistances are measured in electromagnetic units.

The electrostatic value of the capacity C_s is found from the dimensions of the condenser. If a cylindrical condenser is used, C_s may be computed in the following manner. Between the plates of an infinitely long cylindrical condenser, a portion of which is shown in Fig. 1-3, the electric field is everywhere radial. If the charge in electrostatic units per unit length on the cylinders is Q_s, the number of lines of force between the cylinders per unit length is $4\pi Q_s/k'$. At any distance, say r, from the axis, the number of lines of force per unit area, or the field strength, is given by $(4\pi Q_s/k')$ divided by $2\pi r$, or $2Q_s/k'r$. Hence the potential difference between the plates, which is the work necessary to transfer a unit charge from one plate to the other, is given by

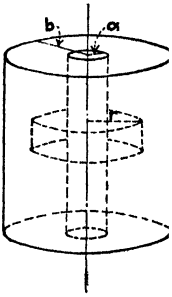

FIG. 1-3.—A part of an infinite cylindrical condenser.

$$V_s = \int E_s dr = \frac{2Q_s}{k'}\int_a^b \frac{dr}{r} = \frac{2Q_s}{k'}\log_e\frac{b}{a}$$

where a and b are the radii of the inner and outer cylinders, respectively. Hence the capacity, with $k' = 1$ for air between the plates, is

$$C_s = \frac{Q_s}{V_s} = \frac{1}{2\log_e\frac{b}{a}}$$

For a condenser of finite length L, the field is no longer strictly radial, and an unknown correction term S must be added to the capacity; *i.e.*:

$$C_s = \frac{L}{2\log_e\frac{b}{a}} + S$$

In order to eliminate the end effect S, two condensers may be used, differing only in their lengths and so presumably having the same value for S. (The rigorous duplication of the end effect is actually very difficult to obtain, as was found by Rosa and Dorsey.) Hence in electrostatic units,

$$(C_1 - C_2)_s = \frac{L_1 - L_2}{2 \log_e \dfrac{b}{a}}$$

The quantity $(C_1 - C_2)_m$ is found from Eq. (1-16) by balancing each condenser separately in the bridge. The ratio of the units is then obtained by applying Eq. (1-1), giving

$$c = \sqrt{\frac{(C_1 - C_2)_s}{(C_1 - C_2)_m}}$$

Satisfactory condensers may be made from two sizes of brass tubing 2 or 3 in. in diameter, with a clearance between the outside of the smaller tube and the inside of the larger of from $\frac{1}{8}$ to $\frac{1}{16}$ in. The cylinders for the larger condenser may be conveniently made about 1 ft. long and those for the smaller one about half that length. The ends may be supported by square bakelite sheets into each of which a circular groove is turned, its larger diameter being equal to the outside diameter of the larger tube and its smaller diameter equal to the inside diameter of the smaller tube. A long brass bolt passing centrally down the tubes is used to clamp the ends firmly to the cylinders. The connecting wires should be soldered to the outside and inside of the large and small tubes, respectively, and go to binding posts on the bakelite ends. The switching device may consist of three platinum contacts, two of them stationary and the center one on the prong of an electrically driven tuning fork, which should have a frequency of at least 100 cycles per second. The resistances R_1 and R_3 should be high, non-inductive resistances of the order of 10,000 to 100,000 ohms, while R_2 may be the ordinary type of plug resistance box. For acceptable accuracy, the potential applied to the bridge should be about 100 volts. If the condensers are accurately constructed and if the bridge measurements are made with care, an accuracy of a fraction of 1 per cent may be attained. Corrections of the results to vacuum and absolute ohms are trivial, for they are much smaller than the probable errors involved.

1-7. Experimental Evidence of the Velocity of Light.—The first successful measurement of the velocity of light was made by Roemer[1] in 1676 from observations on the eclipses of the satellites of the planet Jupiter as they pass into its shadow. It was noted that these eclipses were ahead or behind schedule at 6-month intervals, when the distance of Jupiter from the earth varied by the diameter of the earth's orbit. These discrepancies in the time were explained by Roemer as due to the

[1] ROEMER, *Mém. de l'Acad. des Sciences*, **10**, 399 (1676).

interval required for light to travel the diameter of the earth's orbit, and with the figure then available he calculated the velocity of light to be 2.92×10^{10} cm. per second. Bradley,[1] in 1728, explained the apparent annual shift in the position of the stars by the suggestion that the observed vector velocity of the light from a star is the resultant of the velocity of the star light in space and the velocity of the earth in its orbit. From a knowledge of the latter and the apparent angular displacement of the star, he obtained a value for c in substantial agreement with Roemer's. The result, with more modern values of the aberration angle and the earth's velocity, is 2.9904×10^{10} cm. per second.

Fizeau[2] made the first terrestrial measurement of the velocity of light in 1849. In his apparatus a beam of light passed between the teeth of a rotating cogwheel, parallel to its axis, and then to a distant mirror from which it was reflected back along its path. It then passed through the teeth in the reverse direction and struck a semisilvered inclined mirror and thence was deflected to the observer at one side. If the wheel revolved at such a speed that the train of waves which passed between two teeth on the outward journey returned to find its path blocked by a tooth, no light was seen by the observer. Successive eclipses were observed as the wheel's speed was increased. In practice, however, only minima of intensity are observed, owing to the finite width of the teeth and to the fact that the field of view is constantly illuminated by light reflected from the teeth themselves, unless they are beveled and blackened. Great uniformity of size and spacing of the teeth is essential.

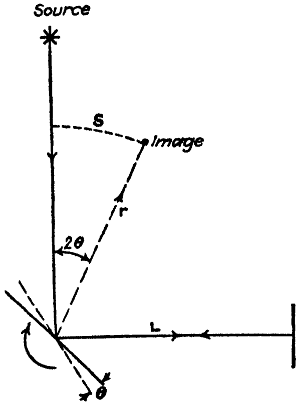

FIG. 1-4.—The principle of Foucault's rotating-mirror method for measuring the velocity of light.

Foucault's method,[3] introduced in 1862, has proved to be the most precise. This method is illustrated diagrammatically in Fig. 1-4. The light is reflected from a rotating mirror to a fixed mirror, L cm. away, and thence back to the rotating one, which meanwhile has turned through an angle θ, so that the returning light is not reflected directly back to the source but is deflected through an angle 2θ to one side. If the mirror is turning at the rate of N r.p.s., or $2\pi N$ radians per second, the time required for it to turn through θ radians is $\theta/2\pi N$ sec. This is also the time required for the light to travel the distance $2L$ at the velocity c, or $2L/c$ sec. Equating these times we have $\theta/2\pi N = 2L/c$. We may put

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[1] BRADLEY, *Phil. Trans. Roy. Soc.*, No. 406 (1728).

[2] FIZEAU, *Comptes Rendus*, **29**, 90 (1849).

[3] FOUCAULT, *Comptes Rendus*, **55**, 501 (1862).

$2\theta = s/r$; where r is the distance from the rotating mirror to the point where the return image is formed in space, and s is the lateral displacement of the image at this distance, so that

$$c = \frac{8\pi NLr}{s} \tag{1-17}$$

The latest and most exact determination of the velocity of light was made by Michelson[1] in 1926, using a modified Foucault apparatus as is shown diagrammatically in Fig. 1-5. Light from the source S was reflected from one face of a rotating octagonal mirror (about 6 cm. in diameter) which was driven by compressed air, and from there to the plane mirrors a and b, the latter being at the principal focus of the 40-in. concave mirror M. From this mirror it traveled 22 miles to a similar mirror M' at the focus of which was a small concave mirror which returned the light *via* M' and M to the plane mirror c (slightly above b). From c it was reflected to d and thence to the opposite side of the octagonal mirror and through a prism into the observing microscope. The angles between the faces of the octagonal mirror were very accurately the same, so that if it rotated through one-eighth of a turn in the time required for the light to make its journey to and fro, the image would be seen in the microscope at exactly the same position as if the mirror had been at rest.

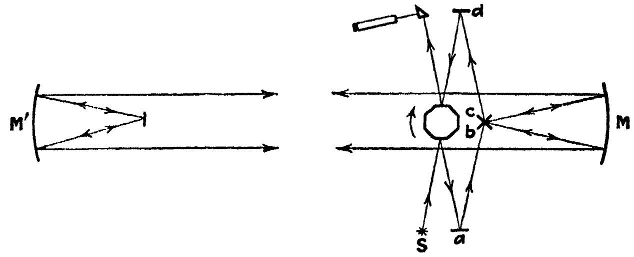

FIG. 1-5.—Diagrammatic sketch of Michelson's apparatus for measuring the velocity of light.

The speed of the rotor (528 r.p.s.) was found stroboscopically by observing it in a small mirror on the tip of an electrically driven tuning fork. The frequency of the fork was verified in a similar manner by a beam of light reflected from a mirror on a pendulum and brought to a focus in the plane of one edge of the fork. The period of the pendulum, corrected for temperature, was compared with a chronometer, the rate of which was determined by radio time signals. It would not have been convenient to measure the speed of the rotor if it had been altered till no displacement of the image was observed, so the timing devices and mirror speed were adjusted to the proper value to give no displacement of the image if light actually traveled with exactly the best previously known velocity, and the position of the image was noted at this standard speed. The direction of rotation of the octagonal mirror was then reversed, and the image position again recorded at the same speed. Half the difference between these values then gave a measure of the rotation of the mirror greater or less than the eighth of 360° required for the image not to be displaced at all. The angular displacement observed in this procedure, which is almost a null method, was very small (0.002 radian), and hence an extremely accurate determination of the distance of the image from the rotating mirror was not necessary. The distance between the two stations (35,385.53 meters) was measured by the U. S. Coast and Geodetic Survey to 1 part in 6.8×10^6. From a knowledge of the index of refraction of air, Michelson corrected the observed velocity to the value it would have in a vacuum, obtaining

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[1] MICHELSON, *Astrophys. J.*, **65**, 1 (1927).

$$c = (2.99796 \pm 0.00004) \times 10^{10} \text{ cm. sec.}^{-1}$$

Birge,[1] in his critical discussion of the general physical constants, remarks that, since Michelson's latest value for the velocity of light and Rosa and Dorsey's value for the ratio of the units agree within their experimental errors, "It seems unlikely that a more accurate value of the velocity of light, c, will be required for some years to come . . . The probable error in c is far less than that in any of the other constants."

Another interesting method of measuring the velocity of light, which has been developed by a number of workers on this subject,[2] is an electrical modification of Fizeau's wheel. Instead of interrupting the light beam with the teeth of a cogwheel, electro-optical shutters are used. These consist of Nicol prisms and Kerr cells. The latter are parallel-plate condensers filled with a liquid, such as nitrobenzene, which causes a rotation of the plane of polarization of light passing through it when an electric field exists between the plates. The Kerr cells are actuated by an oscillator of known frequency. In principle, light passes through the first Nicol prism and Kerr cell only when the electric field is on; it then travels some distance to a second Nicol and cell and can get through only if the next electric cycle has been reached. Successive extinctions of the light passing through the two units are observed as the frequency of the oscillator is varied. This method is capable of great accuracy.

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[1] BIRGE, *Phys. Rev. Suppl.* (*Rev. Mod. Phys.*), **1**, 67 (1929).

[2] KAROLUS and MITTELSTAEDT, *Physik. Zeits.*, **29**, 698 (1928).

MITTELSTAEDT, *Physik. Zeits.*, **30**, 165 (1929).

GUTTON, *Comptes Rendus*, **128**, 1508 (1899); **152**, 685, 1089 (1911); **153**, 1002 (1911); *J. Physique*, **2**, 196 (1912).

GAVIOLA, *Zeits. Physik*, **35**, 748 (1926); **42**, 853 (1927); *Ann. Physik*, **81**, 681 (1926).

The following table[1] gives the final results of various experimenters:

Year	Experimenters	Method	Distance	Velocity, km. sec.$^{-1}$
1849	Fizeau[2]	Toothed wheel	8,633 meters	315,300
1862	Foucault[3]	Rotating mirror	20 meters	298,000 ± 500
1874	Cornu[4]	Toothed wheel	22,910 meters	300,400 ± 300
1874	Cornu-Helmert[5]	Toothed wheel	22,910 meters	299,990 ± 200
1879	Michelson[6]	Rotating mirror	1,968 feet	299,910 ± 50
1882	Michelson[7]	Rotating mirror	2,049 feet	299,853 ± 60
1882	Newcomb[8]	Rotating mirror	3,721 meters	299,860 ± 30
1902	Perrotin[9]	Toothed wheel	45,950 meters	299,901 ± 84
1924	Michelson[10]	Rotating mirror	35,385.53 meters	299,802 ± 30
1926	Michelson[11]	Rotating mirror	35,385.53 meters	299,796 ± 4
1928	Karolus and Mittelstaedt[12]	Kerr cell	332 meters	299,778 ± 20

1-8. Group Velocity.—It is of interest to consider exactly what is the quantity measured, when the velocity of propagation of a light signal is determined in a medium for which μ is unity but $k = k'/c^2$ where k' is not unity. As the index of refraction, n, is the ratio of the velocity in a vacuum to the velocity in the medium, we have

$$n = \frac{c}{v_{\text{med}}} = \frac{c}{c/\sqrt{k'}} = \sqrt{k'}$$

The effective dielectric constant, and therefore the velocity are generally functions of the wave length. Such a medium is known as dispersive. For a variety of reasons, in any experimental determination of the velocity, many different wave lengths are always present: the light used is rarely strictly monochromatic; reflection from a rotating mirror introduces a change in wave length due to the Doppler effect; and, finally, what is measured is a signal—a finite group of waves with a beginning and an end. Such an isolated wave train, even if it is emitted by a source as a pure monochromatic wave, can be represented by a Fourier series of infinitely long wave trains of different frequencies, which cancel each other out except in the region occupied by the signal at any instant. As will be shown, the velocity with which this group advances is not that of the individual waves comprising it.

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[1] Gheury de Bray, *Nature*, **120**, 602 (1927).

[2] Fizeau, *Comptes Rendus*, **29**, 90 (1849).

[3] Foucault, *Comptes Rendus*, **55**, 501 (1862).

[4] Cornu, *Comptes Rendus*, **79**, 1361 (1874).

[5] Cornu and Helmert, *Astronom. Nachrichten*, **87**, 123 (1876).

[6] Michelson, *Astronom. Papers for Am. Eph. and Naut. Alman.*, **1**, 141 (1881).

[7] Michelson, *Astronom. Papers for Am. Eph. and Naut. Alman.*, **2**, 243 (1891).

[8] Newcomb, *Astronom. Papers for Am. Eph. and Naut. Alman.*, **2**, Part 3, 202.

[9] Perrotin, *Annales de l'Observatoire de Nice*, **11**, A104 (1908).

[10] Michelson, *Astrophys. J.*, **60**, 256 (1924); **65**, 2 (1927).

[11] Michelson, *Astrophys. J.*, **65**, 1 (1927).

[12] Karolus and Mittelstaedt, *Physik. Zeits.*, **29**, 698 (1928).

The situation may be quite well approximated by assuming that we have but two different wave lengths superimposed on each other. In the region where both waves are in phase, we get a resultant maximum disturbance whose amplitude drops off gradually to zero at the places ahead and behind, where the two original sets of waves are out of phase with each other. If both waves advance with the same speed, then obviously this region of maximum resultant amplitude moves along with them; but if, because of dispersion, one of the original wave trains moves faster than the other, the region of maximum disturbance either lags behind or precedes the individual waves. Similarly a signal of any form may be considered to be caused by the constructive interference of a large number of infinite wave trains, and its velocity of propagation is known as the group velocity. It is this group velocity which is measured by any method of measuring the velocity of light, for only within the region embraced by the group is there any amplitude of the disturbance.

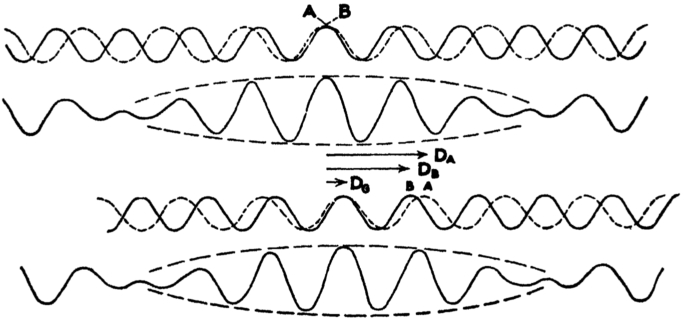

FIG. 1-6.—The phenomenon of group velocity. The two upper figures represent two sine waves of different wave length and their resultant "group wave." The lower figures indicate the same waves after some interval of time, during which a phase wave A of the longer wave length has advanced a distance D_A, while a phase wave B of the shorter wave length has advanced a lesser distance D_B. The group has progressed only the distance D_G. Hence the group velocity is less than either phase velocity. If the short waves had a speed greater than that of the long waves, the group velocity would be greater than either phase velocity.

Let us suppose that there are two sine waves of equal amplitude, A, and with wave lengths λ and λ' traveling with velocities v and v' respectively. The resultant amplitude due to these two waves at any point x and time t is given by

$$y = A \sin \frac{2\pi}{\lambda}(x - vt) + A \sin \frac{2\pi}{\lambda'}(x - v't)$$

From the trigonometric relation, $\sin a + \sin b = 2 \sin \frac{1}{2}(a + b) \cos \frac{1}{2}(a - b)$, we may write

$$y = 2A \sin \pi\left[\left(\frac{1}{\lambda} + \frac{1}{\lambda'}\right)x - \left(\frac{v}{\lambda} + \frac{v'}{\lambda'}\right)t\right] \cos \pi\left[\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right)x - \left(\frac{v}{\lambda} - \frac{v'}{\lambda'}\right)t\right]$$

For only slight differences between λ and λ' and between v and v', we may consider them respectively identical wherever their sums occur and we may write $d\lambda$ and dv for their differences. Thus in this case we have

$$y = 2A \cos \pi\left[d\left(\frac{1}{\lambda}\right)x - d\left(\frac{v}{\lambda}\right)t\right] \sin \frac{2\pi}{\lambda}(x - vt) \tag{1-18}$$

This we recognize as one of the original sine waves with a slowly varying amplitude. This amplitude, which is the amplitude of the group, is itself a cosine wave. If we take the $d(1/\lambda)$ out of the argument of the cosine term, we see that this term is of the form $f(x - ut)$ where

$$u = \frac{d\left(\frac{v}{\lambda}\right)}{d(1/\lambda)} = \frac{\frac{\lambda dv - v d\lambda}{\lambda^2}}{-d\lambda/\lambda^2} = v - \lambda\frac{dv}{d\lambda} \tag{1-19}$$

Therefore the group or signal velocity u is less than the wave or phase velocity v for all transparent media for which v increases with λ. This result may be put in another form. The index of refraction n is given as we have seen by $n = c/v$, where c is the velocity in vacuum and v is the velocity in the medium. Therefore we have:

$$\frac{dv}{d\lambda} = -\frac{c}{n^2}\frac{dn}{d\lambda} = -\frac{v}{n}\frac{dn}{d\lambda}$$

Hence

$$u = v\left(1 + \frac{\lambda}{n}\frac{dn}{d\lambda}\right)$$

and

$$\frac{c}{u} \cong n - \lambda\frac{dn}{d\lambda} \tag{1-20}$$

as is found by substituting for v and then expanding.

Michelson[1] found that the ratio of the velocity of light in air (essentially that in vacuum) to that in carbon bisulphide is 1.77, when yellow light is used. If what is measured is the phase velocity, this should equal the index of refraction. From other measurements n is known to be 1.64; this discrepancy is greater than the experimental error. If, however, it is the group velocity which is measured, then c/u instead of c/v should be equal to 1.77. When the known dispersion, $dn/d\lambda$, for CS_2 is used in Eq. (1-20), almost exact agreement is found. Similar experiments by Gutton[2] on other liquids having large dispersive powers showed experimentally that it is the group velocity which is measured. For air, where the dispersion is small, the group and phase velocities are approximately the same. Further details in connection with this subject are given in the references.[1]

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[1] MICHELSON, *Astronom. Papers for Am. Eph. and Naut. Alman.*, **2**, 235 (1891).

[2] GUTTON, *J. Physique*, 5th series **2**, 196 (1912).

1-9. Experimental Arrangement to Measure the Velocity of Light.—The simplest arrangement of the Foucault method utilizes a rotating mirror with a single face. Light from an arc light or Point-o-lite lamp is focused on a slit or small hole whence it passes through a semisilvered mirror to the rotor. From there it is reflected to a lens of 1 or 2 meters focal length. This distance, from the slit to the rotor to the lens, should be slightly more than the focal length of the lens, so that the image of the slit will be formed at a plane mirror 40 or 50 meters distant. The return image, after reflection from the rotor face and the semisilvered mirror, is formed to one side where it may be observed with a micrometer microscope. This arrangement, if the light retraces its path exactly, is unsatisfactory, for once every revolution, when the face of the rotor is perpendicular to the rays from the source, a brilliant beam is reflected directly back toward the lamp and hence to the observer. Because of the persistence of vision, this flash apparently exists when the much weaker return image appears, and the latter is blotted out. A convenient way to eliminate this difficulty is to replace the single distant mirror by two plane mirrors, inclined at about 90° to each other, their intersection being horizontal. If the light from the slit falls on the lower half of the rotor face and thence is directed to the upper of the two mirrors, it returns from the lower mirror and so strikes the upper half of the rotor face and is reflected to a point slightly above the slit. With proper adjustment,

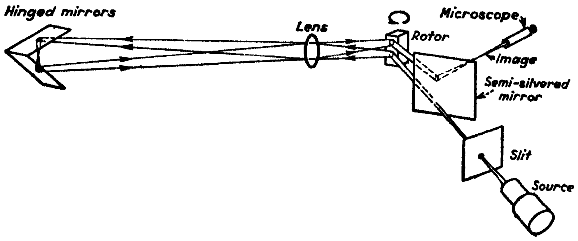

FIG. 1-7.—Arrangement for measuring the velocity of light with two distant mirrors and a rotor having one polished face. Not to scale.

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[1] LADENBURG, *Handbuch der Expt. Physik*, **18,** 1 (1928).

GOUY, *Comptes Rendus*, **91,** 877 (1880); **101,** 502 (1885); **103,** 244 (1886); *J. de Liouville*, 3d series, **8,** 335 (1882); *Ann. de Chim. et de Physique*, 6th series, **16,** 262 (1889).

RAYLEIGH, "The Theory of Sound," 2d ed., Macmillan, vol. I, p. 301 (1894); *Nature*, **24,** 382 (1881); **25,** 52 (1881).

MICHELSON, *Astronom. Papers for Am. Eph. and Naut. Alman.*, **2,** 235 (1891).

GUTTON, *J. Physique*, 5th series, **2,** 196 (1912).

HAVELOCK, "Propagation of Disturbances in Dispersive Media," Cambridge University Press (1914).

the return image will then be seen as a faint line or spot slightly above the undesirable brilliant illumination mentioned before. This arrangement is shown diagrammatically in Fig. 1-7.

A more satisfactory arrangement is to use a rotor with two adjacent polished surfaces at approximately (not necessarily exactly) 90° inclination to one another. (The multifaced mirrors used by Michelson must have the angles between the faces accurately the same, adding greatly to the difficulty and cost of manufacture.) Light from the slit is reflected from one of these faces to the lens and is returned by appropriate means to the other face, whence it passes to the observer, who is thus not troubled by any direct reflection. There are several possible variations of the arrangement to bring the return beam back to the other face of the rotor. Two inclined distant mirrors may be used, but with their intersection vertical as shown in Fig. 1-8, or a single distant mirror may be employed, in conjunction with two small mirrors or prisms placed between the lens and rotor as in Fig. 1-9. This latter arrangement reduces the intensity of the return beam, for one of the mirrors cuts out part of the original light. The maximum intensity will be obtained when the mirror obstructs about one-half of the area of the lens. Due to the increase in path for the return beam between the lens and the rotor, the image is formed closer to the rotor thus diminishing the "lever arm" of the image deflection.

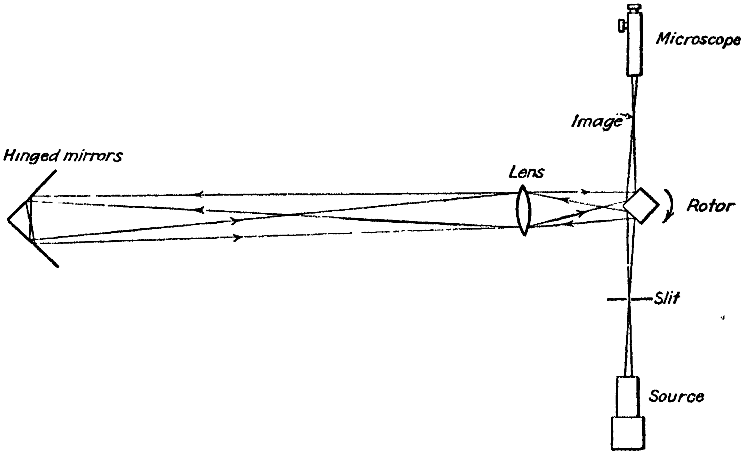

FIG. 1-8.—Arrangement for measuring the velocity of light, using a rotor with two adjacent mirror surfaces and two distant mirrors. Not to scale.

If ordinary-quality lenses and mirrors are used, the observed image of the slit may not be sharp. In that case a black paper pointer or a wire at the distant mirror may be used as a fiducial mark upon which the cross hairs in the observing microscope may be set accurately. It is also possible so to direct the return beam that it illuminates the edge of the rotor nearest to the observer, and the microscope may be focused on this edge. The rotor thus apparently stands still, owing to its stroboscopic illumination, and the cross hairs may be set with great accuracy on its edge. The lateral displacement of the edge for different speeds is, however, very small, since the lever arm is only half the diagonal of the cubical rotor.

The particular arrangement to be used depends largely on the optical equipment available. The distant mirror or mirrors should be preferably front silvered but this is by no means necessary. An ordinary plate-glass mirror does quite well. The lens should have a focal length of at least 1 meter, preferably even greater, and should have as large an area as possible.[1] The rotating mirror may be made of stainless steel, so that the reflecting surface will not deteriorate. The lens may be mounted on a carriage, adapted for vertical and horizontal motion, which slides on an optical bench. The rotating mirror mechanism is then clamped to the far end of the bench. If two distant mirrors are used, they must be mounted in such a way that the angle between them may be slowly and continuously varied, for this adjustment must be made in order to direct the return beam back to the lens at the proper angle. It is also convenient to mount the distant mirrors with some simple slow-motion device to alter their position and orientation. Clamping them to a cathetometer is simple and effective, for the screw feet provide a means of altering the tilt and a change of height or orientation is easily made.

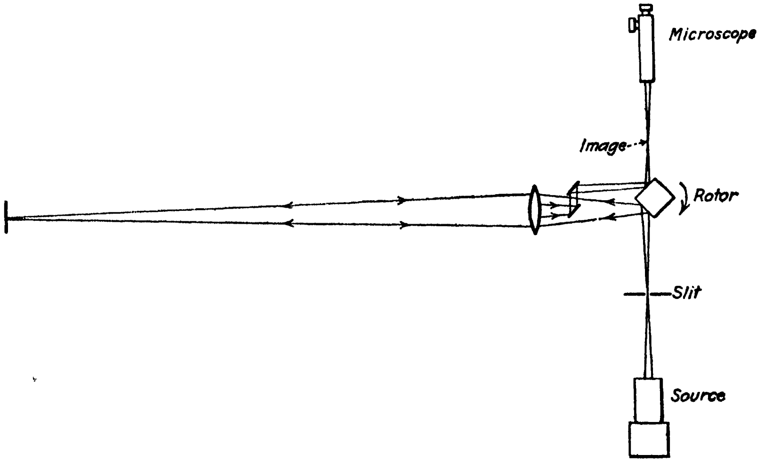

Fig. 1-9.—Arrangement for measuring the velocity of light, using a rotor with two adjacent mirror surfaces, one distant mirror, and two auxiliary mirrors or prisms. Not to scale.

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[1] MICHELSON, "Studies in Optics," University Chicago Press, p. 126 (1927).

To obtain measurable deflections with the light path restricted to a few hundred feet, such as the length of a hallway, high speeds of revolution are required. The method here suggested is that due to Henriot and Huguenard.[1] The construction of a rotor mechanism which has been used successfully is shown in Fig. 1-10. The rotor itself consists of a steel top in the form of a cone about 2 cm. in diameter and 0.8 cm. in altitude. This sits in a steel conical cup of approximately the same dimensions but with a slightly more acute apex angle. Drilled through the walls of the conical seat, approximately one-quarter the way up the slant height and at equal distances from each other, are four holes about 0.5 mm. in diameter which act as jets for the blast of compressed air entering from the surrounding container. The holes lie in vertical planes and point upward at an angle of 45°, so that the four air streams form a whirling jet which both lifts the top and causes it to rotate. The air leaves the region between the two cones with a very high velocity, so by Bernoulli's theorem the pressure on the under side of the cone is less than atmospheric and the top is therefore held in its conical seat. The rotor thus rides without bearings on a cushion of air, in equilibrium under its own weight and the Bernoulli pressure downward and the force of the air blast upward. With an air pressure of 25 to 30 lb. per square inch a speed of 3,000 r.p.s. may readily be obtained. The rotating mirror is made from a four-sided stainless steel block 0.5 cm. on a side and 1.5 cm. high. This block is turned down for about 0.5 cm. at one end and threaded so that it may screw into the center of the rotor. Two adjacent faces of the remaining upper part of the block are polished, and the other two blackened. It is absolutely essential that the top and mirror be made as symmetrical as possible. A certain amount of cut-and-try filing of the unpolished surfaces is generally necessary to permit the combination to ride evenly. It is sometimes necessary to drill out the center of the steel block composing the mirror, to lower the center of gravity sufficiently for stable operation.

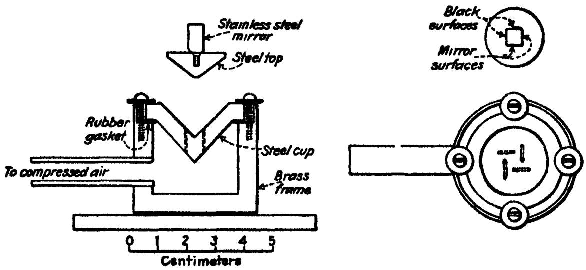

FIG. 1-10.—Sketch of a compressed-air turbine and revolving mirror for measuring the velocity of light. Two adjacent sides of the steel block are ground to mirror surfaces; the other two sides are blackened.

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[1] HENRIOT and HUGUENARD, *J. Physique*, **8**, 433 (1927).

The velocity of rotation of the mirror is determined stroboscopically. For slow speeds, a neon lamp running on the alternating-current power lines may be used; the upper surface of the top is painted white with the exception of a thick black radius. If the lamp is running on a 60-cycle line, it will flash 120 times per second; and if the speed of the rotor is 30 r.p.s., it will turn through one-quarter of a revolution between flashes, and four stationary radii will be observed. Similarly, three radii correspond to 40 r.p.s., two radii to 60 r.p.s., and one radius to 120 r.p.s. Due to the finite time during which the lamp is lighted in each cycle, the black radii appear very fuzzy at high speeds. An electrically driven 100-cycle tuning fork, on one prong of which a very small bit of mirror is mounted with wax, may be used to measure speeds from about 25 to 600 or 800 r.p.s. The side of the rotor is viewed through the mirror, and the rotor apparently comes to rest from time to time as the speed increases. At these speeds the mirror has rotated through some integral multiple of a quarter of a revolution (due to the four sides) during one period of the fork. A 1,000-cycle fork, similarly equipped with a mirror, is needed to detect the speeds of 1,000, 2,000 and 3,000 r.p.s. With a bit of practice one can soon associate the correct speeds with the observed stationary images. Beat notes of the fork with the whistle of the rotor are quite evident and helpful It is desirable, but not necessary, to obtain several readings of the image displacement as the speed is increased and decreased. A better average result is thus obtained.

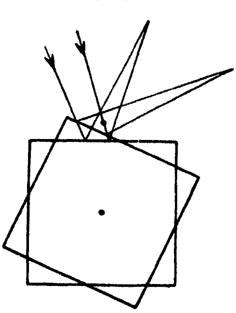

FIG. 1-11.—Reflection of light from a mirror rotating about an axis that lies behind the surface.

If a beam of light is reflected from a mirror that revolves about an axis which lies in its face, the central ray of the beam is deflected through an angle 2θ when the mirror turns through an angle θ, and the point about which the central ray turns lies in the face of the mirror. But when the mirror revolves about an axis which lies behind the reflecting surface, the axis of rotation for the central ray lies in front of the mirror, as shown in Fig. 1-11. Also, the distance from the surface of the mirror to the image is different for different positions of the mirror. The distance of the rotation point from the surface may be shown, by a simple geometrical argument, to be of the order of magnitude of the length of the side of the mirror times θ, the angle between two positions of the surface. Hence for the mirror described above, at 3,000 r.p.s. and with a path length L of 40 meters, θ is only about 0.005 radian, and the error introduced in assuming that the beam rotates about the middle of the face of the mirror is about 0.002 cm. This is quite negligible if the image is formed several centimeters away. The distance of the image from the surface of the mirror may be found by measuring the distance from the center of the surface, when set to reflect light into the microscope, to some mark on the instrument, and subtracting from this the distance from the mark to the focal plane. The observing microscope should have a fairly short focus and shallow field so that these distances can be determined accurately.

We have seen from Eq. (1-17) that the lateral displacement s of the image, distant r from the rotor, is given by

$$s = \frac{8\pi LNr}{c}$$

where L is the distance from the rotor to the mirror and N is the number of revolutions per second of the rotor. If N is varied, we see that we may write

$$\frac{ds}{dN} = \frac{8\pi Lr}{c}$$

It is generally not practicable with the above apparatus to observe the return image when the rotor is stationary, but readings of the image position may be made at a variety of speeds. A graph of the displacement s against the speed N then gives a series of points lying on a straight line the slope of which is $8\pi Lr/c$, so that c may be computed. With a distance of about 40 meters from the lens to the distant mirrors and without correcting for such errors as arise from inaccuracy in the tuning fork, etc., this simple type of apparatus will give consistent results correct to within 1 or 2 per cent.

1-10. Velocity of Propagation of Electromagnetic Waves on Wires.—Under certain conditions the velocity of propagation of electromagnetic waves on wires should equal the velocity of light. If standing waves are set up in a circuit of long straight wires of low resistance in a vacuum or in air, voltage and current loops and nodes will exist on the wires. Their location may be found by various means, and the distance between two consecutive loops or nodes is equal to one-half the wave length. If the period T of the oscillations is known, the velocity may be determined from the relation $\lambda = vT$. The period may be found from the following expression for an oscillating circuit of low resistance: $T = 2\pi\sqrt{LC}$, where L is the inductance and C is the capacity. It may also be found by a series of beat-note comparisons down to some known standard frequency, or by photographing the image of the oscillatory spark as formed by a rotating concave mirror.

The earliest determination of the velocity of these electric waves was attempted by Wheatstone[1] in 1834. He obtained a value for the velocity of 463,000 km. per second. Many others since that time have investigated the problem; among them should be mentioned Hertz[2] who found 200,000 km. per second and Lecher[1] who obtained a result within 2 per cent of the accepted value of the speed of light. Some more recent determinations are:

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[1] Wheatstone, *Phil. Trans. Roy. Soc.*, Part 2, p. 583 (1834).

[2] Hertz, *Wied. Ann.*, **37**, 395 (1889).

Year	Investigators	Velocity, cm. sec.$^{-1}$
1895	Trowbridge and Duane[2]	3.003×10^{10}
1896	Saunders[3]	2.990
1899	MacLean[4]	2.991
1924	Mercier[5]	(2.99700 ± 0.00030)

These values are all in quite good agreement with the observed velocity of propagation of light.

1-11. Wave Aspect of Radiation Pressure.—The existence and magnitude of the pressure of light on the wave conception may be conveniently shown by a method due to Larmor.[6] Let us assume a simple harmonic wave train moving along the positive x-axis toward the origin with the velocity c; the electric force is given by Eq. (1-15)

$$E_y = A \cos \frac{2\pi}{\lambda}(x + ct)$$

Let this wave train fall normally on a perfect reflector advancing with a velocity v, in the positive direction along the x-axis, so that its position at any time is given by $x = vt$. There will then be a reflected wave train traveling in the positive direction given by

$$E_y' = A' \cos \frac{2\pi}{\lambda'}(x - ct)$$

where A' is the reflected wave amplitude and λ' is the wave length. Since a perfect reflector on the electromagnetic theory is a conductor, which cannot support an electric force, the combined disturbance does not enter the reflector and we must have $E_y + E_y' = 0$, when $x = vt$, or

$$A \cos \frac{2\pi t}{\lambda}(v + c) + A' \cos \frac{2\pi t}{\lambda'}(v - c) = 0$$

As this must be true for all values of t, the amplitudes must be equal and the arguments of the cosine functions must be equal in absolute magnitude. So we have $A = A'$, and

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[1] LECHER, *Wien. Ber.* (1890); *Phil. Mag.*, **30**, 128 (1890).

[2] TROWBRIDGE and DUANE, *Am. J. of Sci.* **49**, 297 (1895); *Phil. Mag.*, **40**, 211 (1895).

[3] SAUNDERS, *Phys. Rev.*, **4**, 81 (1896).

[4] MACLEAN, *Phil. Mag.*, **48**, 115 (1899).

[5] MERCIER, *J. Physique*, **5**, 168 (1924).

[6] LARMOR, "Encyclopedia Britannica," vol. 22, 787 (1911).

$$\frac{2\pi}{\lambda}(c+v) = \pm\frac{2\pi}{\lambda'}(c-v)$$

and as the sign is of no significance at this point we may write

$$\frac{\lambda'}{\lambda} = \frac{c-v}{c+v} \tag{1-21}$$

Hence, by reflection at the moving mirror, the wave length is shortened in the ratio $(c - v)/(c + v)$. If we take a unit cross section and a unit length of the incident ray, the kinetic energy in it, which may also be considered as the kinetic energy of the unit volume displaced by the electric force, is equal to $\frac{1}{2}\sigma(dy/dt)^2$, where σ is the density of the medium. As the displacement y is proportional to the electric force, we may write

$$\frac{1}{2}\sigma\left(\frac{dy}{dt}\right)^2 = \frac{1}{2}\frac{\sigma}{a^2}\left(\frac{\partial E_y}{\partial t}\right)^2 = \frac{1}{2}\frac{\sigma}{a^2}\frac{A^2 4\pi^2 c^2}{\lambda^2}\sin^2\frac{2\pi}{\lambda}(x+ct)$$

where a is the constant of proportionality between the force and the displacement. The total energy is given by this expression for the kinetic energy when the potential energy is zero, *i.e.*, when the displacement is zero. This occurs obviously when $\cos\frac{2\pi}{\lambda}(x + ct)$ is zero or when $\sin\frac{2\pi}{\lambda}(x + ct)$ is equal to unity. Therefore the total energy per unit length of the incident wave train is given by

$$\frac{1}{2}\frac{\sigma A^2}{a^2}\frac{4\pi^2 c^2}{\lambda^2}$$

Thus the total energy density of the incident beam is proportional to $1/\lambda^2$, and similarly the energy density in the reflected beam is proportional to $1/\lambda'^2$. Writing E and E' for these energy densities we have:

$$\frac{E'}{E} = \frac{\lambda^2}{\lambda'^2} = \left(\frac{c+v}{c-v}\right)^2$$

In 1 sec., a length $(c + v)$ of the incident wave train moves up to the reflector, and a length $(c - v)$ moves away. The energy striking unit area of the reflector in 1 sec. is thus $E(c + v)$ and the energy reflected is $E'(c - v)$, so the energy moving away is greater than that coming up in the ratio,

$$\frac{E'(c-v)}{E(c+v)} = \left(\frac{c+v}{c-v}\right)^2\frac{(c-v)}{(c+v)} = \frac{c+v}{c-v} \tag{1-22}$$

This increase in energy can come only from the work done by the mirror in advancing against a pressure p, exerted by the radiation. The work done by this pressure in 1 sec. is pv, and hence the energy moving away from the reflector per second is $E'(c - v) = E(c + v) + pv$. Eliminating E' between this expression and Eq. (1-22) we obtain

$$p = 2\frac{c + v}{c - v}E \tag{1-23}$$

From Eq. (1-22) we see that

$$\frac{E + E'}{E} = 2\frac{c^2 + v^2}{(c - v)^2}$$

and by means of this expression we may write Eq. (1-23), in terms of $E + E'$,

$$p = \frac{c^2 - v^2}{c^2 + v^2}(E + E')$$

Thus, if v is small enough so that v^2/c^2 can be neglected, we have

$$p = E + E' \tag{1-24}$$

Therefore the pressure exerted on a plane perfectly reflecting surface by radiation normal to it is equal to the total energy density in front of it. It is also readily seen from the above treatment that this relation is true whether the surface is perfectly reflecting or not. If the surface is a perfect reflector, $E = E'$ and $p = 2E$. If the surface is a black, or perfectly absorbing one, whose emission is negligible ($E' = 0$), the pressure is equal to E. On the assumption of specular reflection from a surface with a reflection coefficient ρ, radiation falling normally on the surface exerts a pressure $(1 + \rho)E$.

If radiation is incident on the surface at an angle θ to the normal, the radiation in unit cross section of the beam falls on an area of $1/\cos\theta$ units of the surface. Therefore the total force per unit area of the surface is $E \cos\theta$, and the normal component of the force is this times $\cos\theta$ or $E \cos^2\theta$. If the radiation falls equally from all directions on one side of the surface (such as is the case for the walls of an enclosure containing isotropic radiation), the pressure is the mean value of $E \cos^2\theta$ taken over all values of the colatitude θ from 0 to $\pi/2$ and of the azimuth ϕ from 0 to 2π. Therefore, as the elementary area on a hemisphere of radius r is $r^2 \sin\theta\, d\theta\, d\phi$, we have

$$p = \frac{E\int_0^{2\pi}\int_0^{\frac{\pi}{2}} r^2 \cos^2\theta \sin\theta\, d\theta\, d\phi}{\int_0^{2\pi}\int_0^{\frac{\pi}{2}} r^2 \sin\theta\, d\theta\, d\phi} = \frac{E}{3} \tag{1-25}$$

Hence the pressure normal to the surface exerted by the incident radiation is equal to one-third the energy density in the incident beam. If the surface is specularly reflecting or if it is a black surface in temperature equilibrium with the incident radiation, the radiation leaving the surface is the same as that falling on it. Hence the pressure exerted by it is also one-third its energy density and the total pressure is equal to one-third the total energy density in front of the surface.

1-12. Particle Concept of Radiation Pressure.—The wave theory of radiation pressure is perfectly satisfactory, and the development of it may be carried through from a more strictly electromagnetic point of view than that of the preceding section. It is, however, of interest to note that the phenomenon may also be explained on the assumption that light consists of particles which are sometimes known as *photons* or *quanta*. As the energy per unit length of a simple harmonic wave train has been seen to be inversely proportional to λ^2, the energy per wave length, λ, or per photon, is inversely proportional to λ or directly proportional to the frequency ν. Let us say that the energy per photon is equal to $h'\nu$, where h', at the moment, is simply some constant.

These photons are moving with the velocity of light, c; and, hence, it is necessary to consider very briefly the theory of relativity, which is of great importance for all very high velocities. On the basis of the principles involved in this theory the mass of a body, which is sensibly constant for all ordinary velocities, actually depends on the velocity of motion of an observer relative to the body in accordance with the expression:

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}} \tag{1-26}$$

Here m_0, which is sometimes known as the rest mass, is the mass which would be measured by an observer at rest with respect to the body, and m is the effective mass as measured by an observer moving relatively to it with a velocity v; c is the velocity of light. The difference between m and m_0 is extremely small for all ordinary velocities; it is less than one part in a million even for velocities as high as 400 km. per second, but, when the speed approaches that of light, Eq. (1-26) becomes of great significance. The derivation of this equation and the experimental evidence in support of it may be found in treatises on the theory of relativity.

On the basis of this dependence of mass on velocity we may calculate, from the Newtonian form of the equations of motion, the relativistic expression for the kinetic energy. The momentum, which we shall write as p, is by definition equal to the mass times the velocity. Therefore the momentum, as measured by an observer moving relatively to it with a velocity v, of a body with a rest mass m_0, is given by

$$p = mv = \frac{m_0 v}{\sqrt{1 - \frac{v^2}{c^2}}} \tag{1-27}$$

The Newtonian statement of the fundamental law of mechanics is that the rate of change of momentum is equal to the applied force, *i.e.*,

$$\frac{d}{dt}(mv) = F \tag{1-28}$$

Let us consider the motion of a body along the x-axis and let us assume that the force F is derivable from a potential-energy function ϕ. The force in the x direction is then given by $F_x = -d\phi/dx$. Using the expression for mv given by Eq. (1-27) and writing the force in terms of the derivative of the potential-energy function, Eq. (1-28) becomes

$$\frac{d}{dt}\left(\frac{m_0 v}{\sqrt{1-\frac{v^2}{c^2}}}\right) = -\frac{d\phi}{dx} \tag{1-29}$$

If we multiply both sides of this equation by v, writing it as dx/dt on the right-hand side, and perform the indicated differentiation, we arrive at the expression

$$v\left[\frac{m_0}{\left(1-\frac{v^2}{c^2}\right)^{\frac{1}{2}}}\frac{dv}{dt} + \frac{m_0}{\left(1-\frac{v^2}{c^2}\right)^{\frac{3}{2}}}\frac{v^2}{c^2}\frac{dv}{dt}\right] = -\frac{d\phi}{dx}\frac{dx}{dt}$$

Taking $\left(1-\frac{v^2}{c^2}\right)^{\frac{3}{2}}$ outside the bracket, we obtain

$$\frac{m_0}{\left(1-\frac{v^2}{c^2}\right)^{\frac{3}{2}}} v\frac{dv}{dt} = -\frac{d\phi}{dt}$$

This we may write as

$$\frac{d}{dt}\left[\frac{m_0 c^2}{\left(1-\frac{v^2}{c^2}\right)^{\frac{1}{2}}}\right] = -\frac{d\phi}{dt}$$

or

$$\frac{d}{dt}\left[\frac{m_0 c^2}{\sqrt{1-\frac{v^2}{c^2}}} + \phi\right] = 0$$

or by Eq. (1-26)

$$\frac{d}{dt}(mc^2 + \phi) = 0 \tag{1-30}$$

Eq. (1-30) shows that the quantity inside the parentheses is a constant. The second term is the potential energy ϕ, and, if mc^2 is interpreted as the kinetic energy, Eq. (1-30) is simply the general expression for the conservation of energy. Thus the theory of relativity leads to the interpretation of the following quantity as the kinetic energy:

$$E = mc^2 = \frac{m_0 c^2}{\sqrt{1-\frac{v^2}{c^2}}} \tag{1-31}$$

For small values of v this must reduce to the familiar value of the kinetic energy plus, possibly, some term independent of the time, for only changes in energy can be measured physically and a constant term may always be present. If we expand Eq. (1-31) in powers of v^2/c^2 and neglect terms containing fourth and higher powers of v/c, we obtain

$$E = m_0c^2 + \tfrac{1}{2}m_0v^2$$

The second term is the ordinary expression for the kinetic energy, and the first term, which is a constant, may be considered as the constant "rest energy." Thus, on the theory of relativity, energy and mass are very intimately connected. As may be seen from Eq. (1-31), the laws of the conservation of energy and mass are identical. When energy spontaneously appears, as in a radioactive process, there must be a corresponding decrease in mass. A gram of radium which generates energy in the form of heat at the rate of about 100 cal. per hour must decrease in weight by about 5×10^{-8} gram per year. As is discussed in a later chapter this conception may be used to calculate the energy of formation of atomic nuclei in terms of their masses and the masses of the component parts from which they presumably are formed. The energy liberated upon the disappearance of mass may possibly be radiated away in the form of a highly penetrating electromagnetic radiation. This is one of the interpretations of cosmic rays, which are a source of ionization in the earth's atmosphere.

Returning to the case of photons, the velocity with which they travel is the velocity of light. If the energy is finite and equal, as we have seen, to a constant times the frequency, we must have their mass m_0 approach zero in such a way that, as v approaches c, E approaches the value $h'\nu$; *i.e.*, $m_0\Big/\sqrt{1 - \frac{v^2}{c^2}}$ is finite, and we may eliminate it between Eqs. (1-27) and (1-31), obtaining

$$p = E\frac{(v)_{v\to c}}{c^2} = \frac{E}{c} \tag{1-32}$$

Hence the momentum of a photon is equal to its energy divided by its velocity. This process, of course, is not legitimate unless $m_0\Big/\sqrt{1 - \frac{v^2}{c^2}}$ remains finite as v approaches c. In the case of a particle with a finite rest mass m_0, the mass m approaches infinity as v approaches c. We may now consider a stream of photons composing a beam of light impinging normally upon a perfectly reflecting surface. If $\rho/2$ is the density of the photons in the incident beam, twice this, or ρ, is the photon density in front of the surface. The number of photons striking the surface per second is $\rho/2$ times the velocity or $\rho c/2$. The change of momentum per photon is $2h'\nu/c$, so the pressure exerted by the beam, which is the rate of change of momentum per unit area, is $\rho h'\nu$. But $h'\nu$ is the energy of a photon, so $\rho h'\nu$ is the energy density in front of the surface. Thus we have the same result as was obtained on the wave theory. This conception of light as discrete quanta or photons will be elaborated in later chapters. It will be seen that the quantum theory predicts that the quantity h' cannot have an arbitrary value, but that it is a fundamental constant of nature, generally written as h and known as Planck's constant.

1-13. Experimental Evidence on the Pressure of Radiation.—As early as 1619, Kepler suggested that the solar repulsion of the finely divided matter composing the tails of comets was due to the force exerted on it by radiation from the sun. In the first half of the eighteenth century De Mairan and Du Fay[1] endeavored to detect the pressure exerted by light, but they were balked by the disturbing action of the gases surrounding the illuminated bodies used in their experiments. This undesired "radiometer effect," which may be either a pressure or a suction on the body, has subsequently been found to be caused by the action of the molecules of the gas. It depends on temperature differences between different parts of the body and between the body and the surrounding medium, caused by absorption of some of the light falling on it. The cause of the effect is not so simple as is generally indicated in elementary treatments, and the mechanism of interaction which is assumed, to explain the phenomena observed, depends on the gas pressure. Knudsen[2] has developed a theory for pressures so low that the mean free path of a molecule is comparable with the dimensions of the radiometer vane and enclosing vessel. Einstein[3] has advanced a theory for the action at much higher pressures, wherein the deflection of the vane is proportional to the moment of the edges of the vane about the rotation axis, rather than to the moment of the area. This theory has received rough quantitative confirmation from the experiments of Marsh.[4] The magnitude of the radiometer forces under some conditions of pressure are enormously greater than the radiation pressure, so that it is not feasible to make a computed correction from the relatively incomplete theory. It is necessary to eliminate the radiometer effect experimentally.

The presence of this effect defeated all attempts to measure radiation pressure until 1901, when Lebedew,[5] and almost simultaneously Nichols and Hull,[6] succeeded in measuring it and in showing that it was equal to the energy density of the light to within their experimental error. Lebedew endeavored to eliminate the radiometer effect by working at low gas pressures (lower than 10^{-3} mm. Hg). As the disturbing action depends on the temperature difference between the illuminated and dark sides of the vane, it would therefore depend on the thickness of two vanes otherwise similar, and hence an estimate of its value could be obtained by the use of vanes of different thicknesses. In his experiments, vanes of different thicknesses made of platinum, aluminium, nickel, and mica (some platinized and some not) were used. The energy in the light beam was determined by noting the rise in temperature of a copper block inside a calorimeter when illuminated for several minutes. The use of a light filter showed that the radiation pressure was independent of wave length. Also, rough measurements of the reflection coefficients of the vanes for the incident light were made, for as we have seen this factor enters the ratio between the pressure and the energy density. The disagreement between the predicted and experimental value was about 20 per cent.

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[1] De Mairan, "Traité Physique et Historique de l'Aurore Boréal," 2d. ed. p. 357, Impr. Royale (1754).

[2] Knudsen, *Ann. Physik*, **32**, 809 (1910).

[3] Einstein, *Zeits. Physik*, **27**, 1 (1924).

[4] Marsh, *J. Optical Soc. Am.*, **11**, 257 (1925).

[5] Lebedew, *Rapportes Presentès au Congrès International de Physique*, (2), 133, (1900); *Ann. Physik*, **6**, 433 (1901).

[6] Nichols and Hull, *Science*, **14**, 588 (1901); *Phys. Rev.*, **13**, 307 (1901); **17**, 26, 91 (1903); *Ann. Physik*, **12**, 225 (1903). Hull, *Phys. Rev.* **20**, 292 (1905).

Nichols and Hull worked at certain rather high gas pressures where the radiometer effect was found to be small. In their experiments a glass vane was used which was coated on one side with highly polished silver. When this was illuminated on the silver side, the moment of the light pressure and the gas action combined was equal to the torque in the suspension fiber, when the steady balance was reached. The suspension was then reversed so that the light fell on the glass surface first. Since the light had passed through several lenses and windows, all wave lengths absorbed by glass had been almost completely removed from the beam by the time it reached the vane, so the silver-coated side always absorbed more energy than the other side and was therefore at a higher temperature, irrespective of the direction of illumination. The radiation pressure was always away from the source for both orientations of the vane whereas the gas action was exerted mainly on the silvered side, so these forces opposed one another in one position and assisted one another in the other. In this way the radiometer effect and light pressure could be distinguished and studied separately as the gas density was varied. The gas forces were repulsive beginning at 66 mm. Hg and changed to suction between 20 and 11 mm., reaching a maximum at 0.05 mm. and becoming a strong repulsion again at 0.02 mm. At certain points in the pressure ranges 20 to 11 and 0.05 to 0.02 mm. the radiometer effect was very small. As the radiation pressure acts instantly and the radiometer effect requires time for temperature differences to be set up, Nichols and Hull still further reduced the opportunity for radiometer forces to come into action by illuminating the vane for short intervals separated by the natural period of rotation of the vane, thus making ballistic rather than static measurements. The energy density of the light beam was determined by letting it fall on a blackened silver disk of known mass and specific heat and by observing its rate of increase of temperature by means of thermocouples imbedded in it. That the pressure was independent of the wave length was demonstrated by passing the light through air, red glass, or a water cell before it fell either on the vane or on the disk. Very careful measurements were made to determine the reflection coefficients of the silver vane for the various wave lengths used.

The results obtained through the following substances were

Substance	Pressure, dynes · cm.$^{-2}$	Energy density, erg · cm.$^{-3}$	Error, per cent
Air	$(7.01 \pm 0.02) \times 10^{-5}$	$(7.05 \pm 0.03) \times 10^{-5}$	0.6
Red glass	(6.94 ± 0.02)	(6.86 ± 0.03)	1.1
Water	(6.52 ± 0.03)	(6.48 ± 0.04)	0.6

1-14. Experiment on Light Pressure.—The experimental verification of the prediction that the pressure exerted by light is equal to the energy density is performed in two parts: (1) the measurement of the pressure exerted by some particular light source, and (2) the measurement of the energy density of the light from the same source.

Since the measurement of the light pressure is complicated by the presence of the radiometer effect, any observed deflection of a small suspended vane when one side is illuminated may be the combined effect of light pressure and radiometer-effect pressure. At some gas densities, as we have seen, the radiometer effect is very small, so if we can discover at what density the radiometer effect vanishes, we may take the observed deflection at that density as a measure of the light pressure. Hence a so-called radiometer vane is suspended in the same container as the light-pressure vane. The radiometer vane is designed to be particularly sensitive to the radiometer effect, so if we illuminate it and vary the gas density till it shows little or no deflection, we may then be sure that the radiometer effect is extremely small on the light-pressure vane, which is designed to be particularly insensitive to the radiometer effect. We shall assume, then, that we are working at such a density that the radiometer effect is zero. A beam of light, which is approximately cylindrical in shape, and with a diameter equal to the width of the pressure vane, is directed so that it is normal to the vane and tangent internally to its edges as shown in Fig. 1-12. The average force of the light is then applied at a distance, $r = (l_1 - l_2)/2$, from the suspension axis of the vane, where l_1 is its length and l_2 its width. Therefore the torque applied to the vane is psr, where p is the light pressure and s is the illuminated area. Under the action of this torque the vane rotates through an angle ϕ radians,

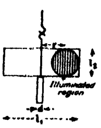

FIG. 1-12. Light pressure vane, showing the area covered by the light beam and the mirror for observing the deflection. Approximately actual size.

at which displacement the torque of the light pressure is equal to the restoring torque of the suspension fiber, $f\phi$, where f is the restoring torque per unit angular displacement. If we can find f and observe ϕ, we can calculate the pressure from the relation

$$p = \frac{f\phi}{sr} \text{ dyne} \cdot \text{cm.}^{-2} \tag{1-33}$$

if s and r are measured in centimeters and f in dyne-centimeters per radian. The angle ϕ is observed with a lamp and scale. Light from a lamp is thrown uniformly on a very small mirror fastened below the vane, whence it is reflected back to a scale, say L cm. from the vane. The uniform illumination of this mirror and its narrowness reduce the possibility of any torque being applied there. Care should be taken that no light destined for the mirror falls on the vane itself. If the main beam of light is directed first on one side of the vane and then symmetrically on the other side, half the difference between the scale readings in centimeters divided by L gives the angle in radians through which the scale beam is deflected. Half of this again is ϕ, the angular deflection of the vane itself. The suspension fiber constant f may be determined from the period T and moment of inertia I of the vane and mirror system. The equation of motion of this system, neglecting damping, when it is rotating under no applied forces, is the simple harmonic equation [see Eq. (1-12)]

$$I\frac{d^2\phi}{dt^2} + f\phi = 0$$

An appropriate solution of this is $\phi = \phi_0 \sin \sqrt{f/I}\, t$, where ϕ_0 is the amplitude. The period is readily seen to be $T = 2\pi\sqrt{I/f}$. I may be computed, for $I = \frac{Ml_1^2}{12} + \frac{md^2}{12}$ where M and m are the masses of the vane and mirror, and l_1 and d are their respective lengths, and all these quantities can be directly measured. Hence, from an observation of the period, f may be computed.

The energy density of the light beam may be measured by observing the rise in temperature of a *black body* of known heat capacity into which the light is directed. Let A calories per second enter a body of mass M grams and specific heat C calories per gram per degree, and let the heat be conducted and radiated away from the body at the rate BT calories per second, where T is the temperature of the body above the surrounding region. (For small temperature differences, both radiation losses and conduction losses along the supports of the body and along the thermocouple wires leading to it may be taken as proportional to the temperature difference.) Then the rate of rise of temperature of the body is:

$$\frac{dT}{dt} = \frac{A}{MC} - \frac{BT}{MC} = \frac{A}{MC} - qT$$

where $q \equiv B/MC$. Writing this in the form

$$\frac{dT}{\frac{A}{MC} - \frac{BT}{MC}} = dt$$

integrating, and determining the constant of integration by the condition that $T = 0$ when $t = 0$, we obtain

$$T = \frac{A}{B}(1 - e^{-qt}) \tag{1-34}$$

One junction of the thermocouple is in contact with the black body and the other remains approximately at room temperature. Hence the above equation gives the temperature difference between the hot and the cold junctions. For small temperature differences the e.m.f. developed is directly proportional to the difference, so we may write

$$E = KT = Ri$$

where E is the e.m.f., K is the thermocouple constant, and $R = (R_c + R_g + R_x)$. Here R_c is the resistance of the thermocouple, R_g that of the galvanometer, and R_x a resistance introduced into the circuit so that $R_c + R_x$ shall be equal to the external critical damping resistance of the galvanometer. The current i produces a couple on the galvanometer coil given by $L = Di$, where D is the galvanometer constant. We thus have $L = DKT/R$ in dyne centimeters, if D is measured in dyne centimeters per ampere, K in volts per degree, and R in ohms.

The equation of motion of the galvanometer coil is similar to that of the light-pressure vane except that there is an appreciable damping force proportional to the angular velocity. Hence we have

$$I\frac{d^2\theta}{dt^2} + j\frac{d\theta}{dt} + g\theta = L$$

or

$$\frac{d^2\theta}{dt^2} + 2a\frac{d\theta}{dt} + b^2\theta = \frac{L}{I} \tag{1-35}$$

where $2a$ is written for j/I, and b^2 for g/I. Here j is the resisting couple, owing to air resistance and electromagnetic damping, for an angular velocity of 1 radian per second and g is the restoring couple per radian displacement of the suspension. When R_x is so chosen that the resistance of the circuit is the critical damping resistance, it may be shown that $a = b$. Introducing this condition and substituting for L and then for T we obtain

$$\frac{d^2\theta}{dt^2} + 2a\frac{d\theta}{dt} + a^2\theta = \frac{DKA}{IRB}(1 - e^{-qt})$$

The solution of this differential equation is:

$$\theta = \frac{DKA}{IRMCq}\left\{\left[\left(\frac{1}{(q-a)^2} - \frac{1}{a^2}\right) - \left(\frac{1}{q-a} + \frac{1}{a}\right)t\right]e^{-at} + \frac{1}{a^2} - \frac{e^{-qt}}{(q-a)^2}\right\}$$

Here B in the coefficient has been replaced by its equivalent qMC.

If the heat losses due to conduction and radiation are very small, we may assume that $q << 1$. Expanding the above expression for θ in powers of q/a, putting $e^{-qt} \cong 1 - qt$, and then setting $q = 0$ we obtain

$$\theta = \frac{DKA}{IRMC}\left[\left(\frac{2}{a^3} + \frac{t}{a^2}\right)e^{-at} - \left(\frac{2}{a^3} - \frac{t}{a^2}\right)\right]$$

The exponential term very rapidly becomes negligible, giving us

$$\theta = \frac{DKA}{IRMC}\left(\frac{t}{a^2} - \frac{2}{a^3}\right)$$

We may differentiate with respect to t and obtain

$$\frac{d\theta}{dt} = \frac{DKA}{IRMCa^2}$$

which is a constant.

The numerical value of this constant may be determined by timing the deflection of the galvanometer with a stop watch, or better still with a chronograph, and applying this equation to the straight part of the curve correlating the galvanometer's deflection with time. The result may be interpreted in terms of the energy falling on the black body, A, if the galvanometer constants and K are known. The latter may be found in tables of physical constants if the thermocouple wires are of pure standard metals. It is better, however, to eliminate the galvanometer constants and K experimentally in the following manner. A test thermocouple of resistance R_t is made from the same materials as the one attached to the black body and in such a shape that each junction may be put in a separate water bath. For a known temperature difference T, between the water baths, the galvanometer comes to a steady deflection θ'', when the restoring torque $g\theta''$ is equal to the applied couple DKT/R', where $R' = R_t + R_g$. Hence the galvanometer deflection per degree difference in temperature between the junctions, θ', is given by

$$\theta' = \frac{\theta''}{T} = \frac{DK}{R'Ia^2}$$

on substituting for g and remembering that $a = b$.

If we divide the rate of deflection of the galvanometer, when connected to the black body, by the thermocouple-galvanometer constant θ', we obtain

$$\frac{1}{\theta'}\frac{d\theta}{dt} = \frac{R'Ia^2}{DK}\frac{DKA}{IRMCa^2}$$

and on solving for A, we obtain the heat input to the black body as

$$A = \frac{R}{R'}\frac{MC}{\theta'}\frac{d\theta}{dt}\ \text{cal. sec.}^{-1}$$

To change A into ergs per second, we multiply this expression by $J(4.18 \times 10^7$ ergs per calorie), the mechanical equivalent of heat. This energy enters the black body in an approximately cylindrical column, of area s, with a velocity c, so the energy density in the incident beam is A/cs, or

$$E = \frac{JRMC}{csR'\theta'}\frac{d\theta}{dt}\ \text{erg}\cdot\text{cm.}^{-3}$$

From this value of the energy density of the incident beam the total energy density in front of the surface can be calculated if the reflection coefficient of the vane is known. The determination of this coefficient is very laborious, and, if the surface of the silver vane is highly polished, the error made in assuming that the reflection coefficient is unity is of the same order of magnitude as the other errors inherent in the experiment. Hence the total energy density, for purposes of comparison with Eq. (1-33), may be taken as twice the incident energy density. Due to the neglect of the reflection coefficient a series of measurements will, on the average, give larger values for the pressure as calculated from the energy density than for the pressure as directly observed.

It has been found by Tear[1] that the successful functioning of a pressure vane depends to a large extent on the shape and material of the container and on the gas which is used. Large thermal capacity, high thermal conductivity, and close proximity of the walls of the container to the vane are important requirements if the gas pressure at which the radiometer effect is negligible is to cover a reasonably large range. Hydrogen is found to be a more satisfactory gas to use than either air or carbon dioxide.

A satisfactory apparatus may be constructed as shown in Fig. 1-13. The container is made from a brass cylinder 3 in. in diameter and 3 in. long, through which two holes about 1.5 cm. in diameter are bored. These holes are enlarged at each end so that they overlap, to insure rapid and uniform gas flow between the chambers. The ends of the block are covered with glass plates and the joints made tight with some suitable vacuum wax. The pressure vane may be made from thin polished silver foil; convenient dimensions are 0.8 by 0.35 by 0.0018 cm. Silver is most satisfactory because it reflects a large fraction of the light striking it, and also, because of its high thermal conductivity and the thinness of the foil, heat which is absorbed is very quickly distributed throughout the vane, thus reducing temperature gradients and the consequent radiometer effect. A fine silver wire is fastened down the center of the vane with very small bits of wax; to the lower end of the wire a small mirror (approximately 0.1 by 0.3 cm.) may be waxed, while the upper

[1] Tear, *J. Optical Soc. Am.*, **11**, 135 (1925).

end is bent into the form of a hook. This must be supported by a very fine quartz electrometer fiber, with metal hooks on each end; the lower hook holds the vane and the upper one engages a stiff copper wire passing through a small hole in the brass plug on top of the container. The plug and wire are made vacuum tight with a suitable wax, *i.e.*, one which has a low enough melting point so that adjustments of the copper wire may readily be made. The suspension constant should be about 5×10^{-5} dyne centimeter per radian, giving a period of oscillation for the vane of 10 or 15 sec. This will give a total deflection on a scale 1 meter away of 10 or 15 cm., when the vane is illuminated first on one side and then on the other by some intense and steady light source such as a Point-o-lite or powerful incandescent lamp. The radiometer vane may be made of two thin rectangular sheets of mica, about 0.8 by 0.35 cm. These are separated in the middle by a vertical wire or fiber, waxed in place, which carries on its lower end a mirror similar to that on the pressure vane. Its upper end hooks into an electrometer fiber mounted in the same manner as the other one. The mica sheets should also be separated at their ends by coarse quartz fibers. The purpose of thus separating the front and back surfaces of the vane is to prevent heat conduction from one face to the other and thus to accentuate temperature differences. The right half of the front vane and the left half of the rear vane are blackened with india ink to increase absorption, as shown in Fig. 1-13. The radiometer vane may alternatively be constructed from a single mica strip. This is almost as satisfactory and it is a little simpler to make.

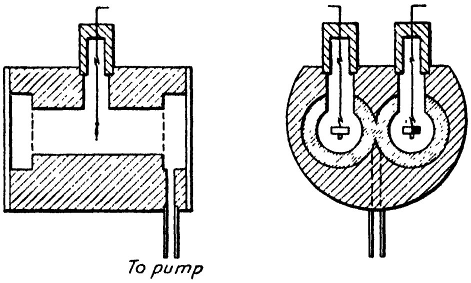

FIG. 1-13.—Light pressure apparatus. About one-third actual size.

The black body for measuring the energy density may be made of the same silver foil from which the pressure vane was cut. A square box about 2 by 2 by 1 cm., its edges sewn together with fine silver wire, is a convenient form. One side is curled inward, as shown in Fig. 1-14, to form a light trap. The mass of the box should be very small and the inside should be washed with india ink or aquadag (an emulsion of carbon and water) so that it will be highly absorbing. The mass of the box must be determined before and after blackening in order to calculate the heat capacity of the silver box itself and of the carbon coating. Camphor black or bismuth black, which are more efficient absorbers of radiation, may be used, but they are more difficult to apply. The box may be supported by an arrangement such as is shown in Fig. 1-14. Two glass hooks, which are part of the supporting framework of glass cane, engage holes in two extensions of the sides of the box. The thermocouple may be made by attaching the ends of fine nickel and iron wires (approximately 0.002 cm. in diameter) to the bottom of the box with a minute drop of solder. The other ends of the wires should be soldered to stiff copper wires fastened to the glass frame; these in turn are brazed to tungsten leads passing through the glass walls of the bulb. This container should be pumped out and the walls torched for several hours

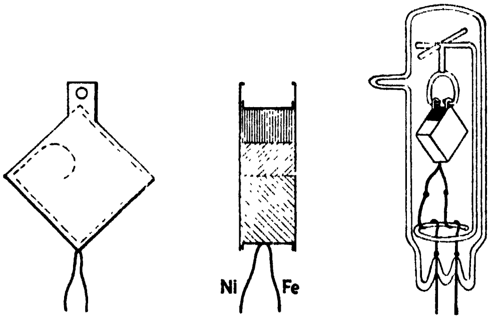

FIG. 1-14.—Silver "black body" to measure the energy density in a light beam. On the right is sketched a method of support in an evacuated bulb. The drawings on the left are approximately full size.

at a pressure of less than 10^{-5} mm. Hg, and then carefully sealed off from the pumping system. The resistance of the thermocouple must be measured and sufficient external resistance introduced into the circuit of the couple and high (voltage) sensitivity galvanometer to produce the critically damped situation.

The test thermocouple is made from pieces of the same nickel and iron wires, mounted on a U-shaped glass rod with one junction at each tip. The wires may be waxed to the glass and should be protected with a coating of glyptal lacquer. Each leg is placed in a beaker of water containing the bulb of a thermometer, reading to hundredths of a degree centigrade. One beaker is left at room temperature, and to the other a small quantity of hot or cold water is added and the mixture thoroughly stirred. Several readings are then taken of both thermometers and of the galvanometer deflection, and the average for each of these quantities calculated. This is necessary, for it is difficult in such a simple apparatus to keep the temperatures constant over any length of time. The temperature of the water bath is then changed by the addition of water at a different temperature and another set of readings taken. This is repeated a number of times to obtain an average value of the galvanometer deflection per degree difference between the thermocouple junctions. The maximum variation from the average should not exceed 5 per cent. The resistance R_t of the test thermocouple must also be measured.

The apparatus is then arranged as shown in Fig. 1-15. The radiometer vane and its mirror are uniformly illuminated by the lamp of a powerful lamp-and-scale combination. The back of the chamber containing this vane should be covered with a black-paper screen to exclude stray light. The mirror of the pressure vane is illuminated by a second lamp, and the light is kept from falling on the vane itself by a suitably placed black-paper screen. Lenses may be used if necessary in front of the vane chambers to form images of the lamp filaments or cross hairs on the scale. A small image of the main light source, the Point-o-lite button or incandescent filament, is formed on a small hole (1 to 2 mm. in diameter) in the screen. An image of this sharply defined hole is then cast on the pressure vane by the lens L and mirror M (preferably front silvered). The latter is arranged to rotate about a vertical axis so that the image may be directed on either limb of the pressure vane or into the black body. An ammeter and a variable resistance should be included in the circuit of the light source so that any fluctuations in the line voltage may be compensated and the current through the lamp kept constant during the experiment. The radiometer deflections will be found to be negligible, and hence the pressure vane deflections independent of the gas pressure, over the range from 40 to 10 cm. Hg, approximately, if hydrogen is used. Thus in this region the deflection which is observed is due to radiation pressure. A typical plot of the pressure vane deflection against gas pressure is given in Fig. 1-16. Air may be used instead of hydrogen, but the results are not quite so satisfactory,[1]

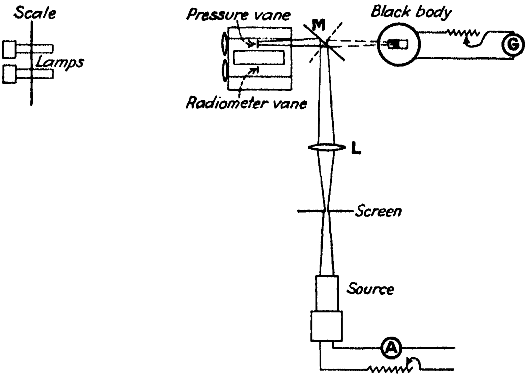

FIG. 1-15.—Apparatus for comparing the pressure and energy density of a light beam.

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[1] TEAR, *J. Optical Soc. Am.*, **11**, 135 (1925).

for the curves are not so closely parallel to the gas-pressure axis. Below 10 cm. Hg the curves are no longer parallel to the axis due to the increasing importance of the radiometer effect. Tear has shown that at very low pressures the radiometer effect again diminishes and an extrapolation of the vane deflections to zero pressure gives a residual deflection equal to that observed at high pressures. It is tedious to work in a high

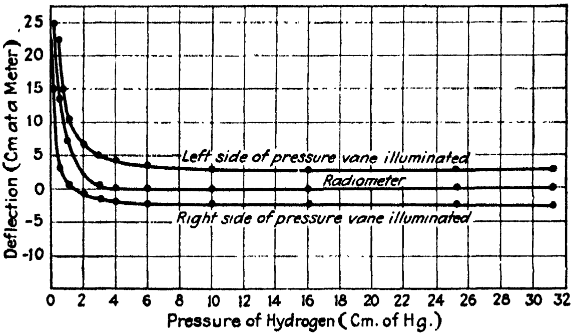

FIG. 1-16.—Graph showing the constancy of the radiation pressure and the absence of any appreciable radiometer effect over a large range of gas pressure. The slight inequality of the right and left pressure vane deflections, in the pressure range where the radiometer effect is small, is due to lack of symmetry in the construction and illumination of the vane.

vacuum, however, for, owing to the very slight damping, the vanes do not come to rest in any convenient time and the deflection has to be found from an average of the limits of oscillation. With reasonable care and working at high pressures, this apparatus is capable of giving an agreement to within a few per cent between the pressure and the energy density of the radiation. Better agreement is not to be expected unless monochromatic light is used and the reflection coefficient for this light is measured.

CHAPTER II

BLACK-BODY RADIATION

2-1. Introduction.—It was mentioned in Chap. I that the electromagnetic theory accounted adequately for all of the many phenomena connected with the propagation of light and of radiant energy in general. It was also seen that this theory predicted the observed value for the velocity of propagation of radiation. But the extension of the electromagnetic theory along classical lines is not adequate to account for the phenomena of emission and absorption of radiation. If we consider the equilibrium situation attained by radiation contained in an enclosure and apply the laws of classical statistical mechanics to this radiation, we are led to an absurdity. It was studies of this type of radiation that first revealed the inadequacy of the classical theories, which had been so ably developed during the preceding century. The revolutionary hypothesis, which was introduced tentatively by Planck to account for the observed phenomena, was accepted and defended by Einstein, and it formed the germ from which have sprung most of the developments of physical theory during the present century.

The radiation which exists inside an enclosure in equilibrium with its walls is characterized by a particular distribution of energy over the total range of wave lengths in the spectrum. This type of radiation is known variously as *black-body, heat, temperature,* or *cavity* radiation. In this chapter we shall briefly develop the thermodynamic theory of this radiation and describe two experiments illustrating its most important conclusions. The result of the first of these experiments is in accord with the thermodynamic predictions based upon the relation, which has been developed previously, between radiation pressure and energy density. The results of the second experiment, dealing with the energy distribution in the spectrum of black-body radiation, while in accord with the incomplete predictions of thermodynamics, are greatly at variance with the predictions of classical statistical mechanics. We shall then consider the changes which are necessary in the classical conceptions to account for the results of these experiments.

The exact mechanism of the emission and absorption of radiation by matter is but little understood. The fundamentally electrical nature of the ultimate particles of matter undoubtedly plays a leading rôle in this energy interchange. It has not been found possible, however, to explain from these electrical particles, and in accordance with the electromagnetic laws the construction of an atomic radiating system which will account satisfactorily for all the observed phenomena of radiation. What success has been achieved in the description of these radiating systems will be discussed later in connection with radiation emitted by the atoms or molecules of gases and vapors when they are suitably excited. In the first part of the present chapter we shall see what progress can be made in the discussion of radiation along thermodynamic lines, without a knowledge of the exact processes of emission and absorption.

2-2. Principles of Thermodynamics.—The subject of thermodynamics is based upon two fundamental physical laws which have been well tested and found to be valid, at least for all large-scale or macroscopic phenomena. The first law is simply the law of the conservation of energy, expressed in such a way as to include energy in the form of heat. A body in a given state has a so-called internal energy associated with it which is a definite function of the variables necessary to completely specify the state of the body. The difference between the internal energies of a body in two states is determined when the values of these variables are known for the two states or when the configurations and motions of the molecules composing the body are known in the two states, assuming such a knowledge to be possible. Therefore the difference between the internal energies is independent of the intervening history of the body. If a quantity of energy in the form of heat, δQ, is added to a body, it will contribute, say, an amount dE to this internal energy, and during the process the body will do an amount of work, let us say, δW. If energy is conserved we shall have the following relation:

$$\delta Q = dE + \delta W \tag{2-1}$$

This may be considered as a statement of the first law of thermodynamics. In this relation the quantities δQ and δW are not to be considered as differentials of functions Q and W, for no such functions exist. The integral of δQ between two physical states is not uniquely determined but depends on the particular manner in which the body passes from one state to the other, *i.e.*, on the path of integration. The same is true for the integral of δW, hence these integrals have no meaning unless the path of integration is specified.

The second law of thermodynamics may be stated in various ways. It is concerned with the tendency of energy to flow down a temperature gradient, *i.e.*, the tendency in nature of heat to flow from a hot to a cold body. A convenient formulation of the law is due to Clausius: "It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature." Such a machine or heat engine is any mechanism whatever capable of the conversion of heat into mechanical energy. On the basis of this law, it may be shown that a function ϕ exists, known as the *entropy*. This is a measure of the unavailable energy in any system and may be defined by the differential relation

$$d\phi = \frac{\delta Q}{T} \tag{2-2}$$

where T is the thermodynamic temperature, which is the same as the *absolute* temperature defined by the perfect gas law, $pv = RT$. Eliminating δQ between Eqs. (2-1) and (2-2), we find

$$Td\phi = dE + \delta W \tag{2-3}$$

If the work done by the thermodynamic substance or engine is against a hydrostatic pressure p, the work δW may be written as pdv, where dv is the change in volume. Dividing Eq. (2-3) by T, we may then write it as

$$d\phi = \frac{dE}{T} + \frac{pdv}{T} \tag{2-4}$$

2-3. Kirchhoff's Law.—We may consider heat radiation, of which the visible light emitted by a glowing filament is a particular example, as simply a mechanism for the transfer of heat from one material body to another. This radiation, of course, possesses the familiar properties of light, such as approximately rectilinear propagation with the characteristic velocity which we have measured. We shall define the particular type of radiation which we have called heat radiation, with which we deal in this chapter, as that radiation emitted by a substance which depends only on the temperature of that particular substance. This differentiates heat radiation from other types of radiation which are less simple, such as the characteristic radiation emitted by gases when stimulated by electron bombardment in a discharge tube or by some other radiation falling on the gas from an external source. Similarly, phosphorescent radiation induced by chemical action is excluded from our consideration. Bodies at all temperatures emit this heat radiation, as may be shown by the decrease in temperature of a body suspended in an evacuated enclosure the walls of which are maintained at a lower temperature. The radiant energy emitted by a body changes only in intensity as the temperature is altered. Thus between the body in the evacuated enclosure and the walls a continual interchange of energy is taking place by means of this radiation. If the body is hotter than the walls, it emits more radiation than it receives and hence its temperature falls; if it is colder than the walls, the converse is true and the temperature of the body rises. The truth of this conception was first recognized by Prevost, and it is known as Prevost's theory of exchanges. The energy in the range of the spectrum which is visible only becomes appreciable to the eye when the temperature of the body is above 500° or 550°C. Heat radiation may be detected by other than optical means at much lower temperatures. A sensitive thermocouple with a blackened junction which absorbs a large fraction of the incident radiation, or even a thermometer with a blackened bulb, will detect radiation from bodies only a few degrees hotter than the detecting instruments.

We shall now briefly discuss the energy interchange between bodies by means of heat radiation, limiting ourselves to substances which are completely opaque, *i.e.*, we shall neglect radiation which can pass directly through any of the bodies with which we deal. This simplifies the discussion and involves little loss of generality, for the energy in heat radiation which can pass through an ordinary opaque substance is in general very small. A more detailed description is to be found in treatises dealing with heat radiation such as those by Kirchhoff,[1] Planck,[2] or Lorentz.[3] Before proceeding to a discussion of this type of radiation, it is necessary to define a few of the quantities which will be used. We shall define the radiant energy leaving a surface element dA of a body and entering a small cone of solid angle $d\omega$, whose axis is normal to the element dA, in a time dt and with a wave length between λ and $\lambda + d\lambda$ as

$$k_\lambda \, d\lambda \, d\omega \, dt \, dA \tag{2-5}$$

This energy is thus considered to be proportional to the solid angle, the time, and the area. The constant k_λ may be considered as the normal monochromatic emissive power, and this will in general depend on the temperature, the nature of the surface, and the particular wave-length range under consideration. If a certain amount of energy in this same wave-length range falls on a surface, a portion of it will be absorbed, and, if transmission is neglected, the remainder will be reflected. The fraction of this energy which is absorbed is called the absorptivity of the surface, and we shall write a_λ for this fraction. The fraction reflected is called the reflectivity, and for this we shall write r_λ. If no change in the energy distribution in the spectrum takes place at the surface, we have the relation $a_\lambda + r_\lambda = 1$.

Now let us consider an evacuated enclosure whose walls are impervious to external radiation. These walls, which may be made of any material we choose, are maintained at a constant temperature. It is convenient to conceive of this enclosure in the form of a large sphere, though this is not essential to the argument at this point. As the heat radiation emitted by an area of the walls depends on the temperature, the energy emitted by equal areas in equal times is the same. In equilibrium this is also equal to the energy absorbed by the area. For if this were not so, and if the walls were not maintained at a constant temperature by an external source, a temperature gradient would be set up, contrary to the second law of thermodynamics. Hence, the energy emitted by a small area to the rest of the walls is equal to the fraction of the energy reaching this area which is absorbed. We shall assume at this point that the energy emitted by an element dA_1 which is absorbed by the element dA_2 is equal to the energy emitted by dA_2 which is absorbed by the element dA_1. This is analogous to the assumption involved later in the chapter, known as the principle of detailed balancing, or the reciprocity theorem. In general, this theorem may be stated as follows: If one elementary process occurs at equilibrium, exactly the reverse process also occurs and just as frequently. If, in the case of the two emitting elements dA_1 and dA_2, the rest of the walls were perfectly reflecting, it could be shown that the energy reaching dA_1 from dA_2 would be equal to the energy reaching dA_2 from dA_1. But as this is not the general case, where the walls are of an arbitrary material, the reciprocity theorem must be assumed. It leads to the so-called cosine law of emission, which is only approximately true for ordinary substances. In actual practice, the departure from the law is greater the greater the angle between the normal to the surface and the direction of emission. If the cosine law, which we will now develop, were not approximately true, the outer portions of the disk which we see when looking at a glowing sphere would appear brighter than the inner portions, which is contrary to experience.

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[1] Kirchhoff, *Ann. Physik u. Chemie*, **49**, 275 (1860).

[2] Planck, "Wärmestrahlung," 5th ed., Barth (1923).

[3] Lorentz, "Lectures on Theoretical Physics," vol. II, Macmillan (1927).

Consider the enclosure represented in Fig. 2-1. Let us assume that we may write for the radiant energy emitted by the element of internal surface dA_2 in unit time and comprised in the wave-length range from λ to $\lambda + d\lambda$, into the solid angle $d\omega_2$ whose axis makes an angle θ_2 with the normal, the expression

$$C_2 k_\lambda \, d\lambda \, d\omega_2 \, dA_2$$

where C_2 is a factor which has been introduced into Eq. (2-5) to take into account any variation of emission with angle. The energy emitted by this area and absorbed by the area dA_1 is this quantity multiplied by a_λ, where the solid angle subtended by dA_1 at dA_2, namely, $dA_1 \cos \theta_1/d^2$ is written for $d\omega_2$. We then have for this quantity

$$C_2 a_\lambda k_\lambda \, d\lambda \frac{dA_1 \, dA_2}{d^2} \cos \theta_1$$

The energy emitted by dA_1 and absorbed by dA_2 in this wave-length range is by a similar argument equal to

$$C_1 a_\lambda k_\lambda \, d\lambda \frac{dA_1 \, dA_2}{d^2} \cos \theta_2$$

If these are to be equal we must have $C_1 = \cos \theta_1$ and $C_2 = \cos \theta_2$. Hence, rewriting the expression in general terms, we see that the energy emitted by a surface element dA in unit time and in this wave-length

range into a solid angle $d\omega$ whose axis makes an angle θ with the normal to the area is given by

$$k_\lambda \, d\lambda \cos \theta \, dA \, d\omega \tag{2-6}$$

which is an expression of the cosine law. From this expression we may obtain the entire monochromatic emissive power which we shall write as $e_\lambda \, d\lambda$. The solid angle $d\omega$, as shown in Fig. 2-2, subtended at the center by the area element $r^2 \sin \theta \, d\theta \, d\phi$ of a hemisphere of radius r, is given by this area divided by the square of the radius, *i.e.*, by $\sin \theta \, d\theta \, d\phi$. Putting this for $d\omega$ and integrating θ from 0 to $\pi/2$ and ϕ from 0 to 2π, *i.e.*, over the surface of the hemisphere, we obtain the total energy emitted by the element dA in this wave-length range, or the monochromatic emissive power times this area element. Performing the integration we obtain:

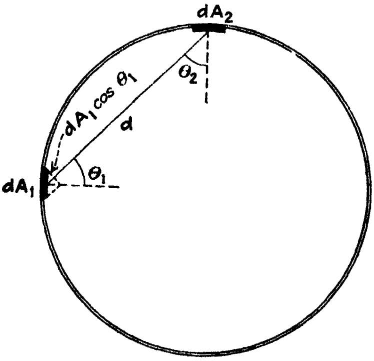

FIG. 2-1.—Radiation between surface elements of a cavity.

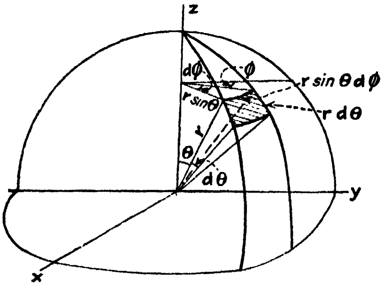

FIG. 2-2.—Solid angle in terms of polar coordinates.

$$\begin{aligned} e_\lambda dA &= k_\lambda \, d\lambda \, dA \int_0^{2\pi} \int_0^{\frac{\pi}{2}} \cos \theta \sin \theta \, d\theta \, d\phi \\ &= k_\lambda \, d\lambda \, dA \, 2\pi \int_0^{\frac{\pi}{2}} \sin \theta \, d(\sin \theta) \\ &= \pi k_\lambda \, d\lambda \, dA \end{aligned} \tag{2-7}$$

Thus the monochromatic emissive power is equal to π times the normal monochromatic emissive power. The total emissive power is of course equal to the integral of the monochromatic emissive power over all wave lengths, so if we write πK for the total emissive power we have:

$$\pi K = \int_0^\infty \pi k_\lambda \, d\lambda = \int_0^\infty e_\lambda \, d\lambda \tag{2-8}$$

Now let us return to the enclosure of Fig. 2-1. If we introduce some body into this enclosure it will come to the same temperature as the walls, when the equilibrium situation is reached. This is obvious, for if it came to some different temperature we could continuously utilize the temperature difference between it and the walls to obtain work by means of a thermodynamic engine, and this is contrary to the second law of thermodynamics. If the body that we introduce is complex, *i.e.*, if its surface is made up of areas of different materials with different emissive powers and absorptivities, we still must have the total energy absorbed by the body equal to the total energy emitted by it when it attains the temperature of the walls; otherwise the temperature of the body after reaching this state would change and its equilibrium temperature would be different from that of the walls. This must be true for all positions and orientations of the body in the enclosure, and, as the absorptivities of its different areas are different, the total absorption can only remain unchanged if the radiation in the enclosure is the same at all positions and in all directions. Hence the radiation in the enclosure is homogeneous and isotropic; *i.e.*, if we again specifically consider the wave-length range from λ to $\lambda + d\lambda$, the energy in this range striking a unit area in a unit time, which we may call $E_\lambda\, d\lambda$, is the same for all positions and orientations of the area. This must of course be true for all wave-length ranges, for in equilibrium there can be no net interchange of energy between two wave lengths. We can also show that this energy is independent of the shape and material of the walls. For let us consider in detail the radiation interchange between a body of monochromatic emissive power $e_\lambda d\lambda$ and absorptivity a_λ and the walls of the enclosure. The energy emitted by the body in this wave-length range per area element dA is $e_\lambda\, d\lambda\, dA$ and the total energy emitted in this range is the integral of this over the body. As the emissive power is taken to be constant, this is $e_\lambda\, d\lambda\, A$ where A is the area of the body. The energy absorbed in this wave-length range is a_λ times $E_\lambda\, d\lambda\, dA$ integrated over the surface of the body, or $a_\lambda E\, d\lambda\, A$ since a_λ and E_λ are constant over the surface. For these to be equal we must have the relation $e_\lambda/a_\lambda = E_\lambda$. If the body were placed in an enclosure at the same temperature so that a_λ and e_λ were the same, but having walls of a different shape and composed of different materials, we would have in equilibrium the similar relation $e_\lambda/a_\lambda = E_\lambda'$, where $E_\lambda'\, d\lambda$ is the energy in the wave-length range striking a unit surface in a unit time in the second enclosure. But as the left-hand sides of these two expressions are the same, we must have $E_\lambda = E_\lambda'$, and hence this quantity is independent of the shape or material of the walls. We may also see that if we had a body which absorbed all the energy which was incident upon it in this wave-length range, we should have $a_\lambda{}^b = 1$ and $r_\lambda{}^b = 0$; hence, if such a body were contained in the enclosure, we would have

$$e_\lambda{}^b = E_\lambda. \tag{2-9}$$

Such a body is known as a "black body" by analogy with the known characteristics of a body which appears black for visible light. We may thus write the following relation, which is known as Kirchhoff's law:

$$\frac{e_\lambda}{a_\lambda} = e_\lambda{}^b \tag{2-10}$$

This relation may be stated in words by saying that the ratio of the emissive power to the absorptivity is the same for all bodies at the same temperature and is equal to the emissive power of a black body at this temperature. This is a law of great significance. It shows that no body can emit radiant energy at a greater rate than a black body, for the maximum value of a_λ, namely that possessed by a black body, is unity; and any smaller value of a_λ would imply a smaller value of e_λ by Eq. (2-10). Hence, the black body, which is the most efficient absorber, is also the most efficient emitter.

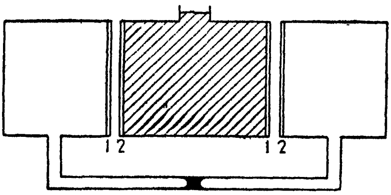

FIG. 2-3.—Ritchie's apparatus to demonstrate Kirchhoff's law.

The content of this law was known before the time of Kirchhoff, and, in fact, as early as 1833 an experiment was performed by Ritchie[1] which showed that Eq. (2-10) when integrated over all wave lengths was true. In his experiment a cube with two of its faces covered with different materials was placed between two gas-filled chambers whose two surfaces facing the cube were composed of the same materials as the surfaces of the cube which were not directly opposite them. These chambers were connected by a tube containing a drop of fluid which would move in the direction of decreasing pressure if any alteration of the pressures in the chambers occurred. The apparatus is shown schematically in Fig. 2-3. The temperature of the cube could be altered by filling it with water at various temperatures. When this was done, no motion of the fluid drop was observed. This was true whatever the surfaces labeled 1 and 2 in the diagram were composed of, as long as the surfaces with the same numbers were of the same material. Since the drop did not move, the pressures in the two chambers were altered equally; hence the temperatures of the gases in the two chambers were also changed by equal amounts. This could only be true if the radiation emitted by surface 1 and absorbed by 2 was equal to the radiation emitted by surface 2 and absorbed by 1. If E is the energy emitted by a surface, and A the fraction of the incident energy absorbed by the surface, we must have

$$E_1A_2 = E_2A_1$$

If the surfaces labeled 2 were black, we would obtain $E_1/A_1 = E^b$, which is essentially Eq. (2-10) integrated over all wave lengths. This general property of surfaces may be very strikingly demonstrated by painting a design on a piece of white china with a heat-resisting black paint, such as one containing manganese dioxide, and then raising the temperature of this surface. The phenomena observed may be analyzed in the following way. If the subscripts w and b refer to the white and black surfaces, the radiation leaving the white portion is $E_w + R_wQ$ or $E_w + (1 - A_w)Q$, where R_w and A_w are the reflectivity and absorptivity, respectively, for all wave lengths, and where Q is the radiation reaching the surface from any light source in the room. Similarly, the light leaving the black area is $E_b + (1 - A_b)Q$. Hence the difference between the amount of light leaving the white and black areas is

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[1] RITCHIE, *Ann. Physik u. Chemie*, **28**, 378 (1833).

$$(E_w - E_b) + (A_b - A_w)Q$$

or

$$(A_b - A_w)(Q - E_b)$$

Therefore, if $A_b > A_w$, the white portion will appear brighter than the dark area if $Q > E_b$, whereas the black area will appear brighter if $Q < E_b$. Hence, if the temperature is held constant so that E_b remains the same, and if the illumination in the room is increased, first the black portion and then the white will seem to be brighter, and the two will be indistinguishable at the time when $Q = E_b$. Or if the illumination Q is kept the same and the temperature raised, first the white and then the black regions will appear to be brighter, for E_b rises with the temperature. It is obvious that the black regions do not have to be "black" in the thermodynamic sense; it is only necessary that $A_b > A_w$.

A more detailed experimental verification of this law was performed by Pfluger,[1] who measured the emission and absorption of a thin crystal of tourmaline for radiation polarized in different directions. He found that these quantities a and e for the two characteristic planes of polarization obeyed Kirchhoff's law. In the above discussion, the question of the polarization of the radiation has not been mentioned, but that this experimental result should be expected is shown in the more complete treatments of the subject to which reference has been made. The predictions of Kirchhoff's law are further verified in the phenomena of absorption and emission of the line spectra of gases. For if a salt is introduced into a flame, or if an electric arc is maintained through the metallic vapor between two electrodes, the emitted light, when analyzed by a spectroscope, is found to be composed of bright lines which are characteristic of the substance which is being vaporized. If light of all colors is passed through the flame or arc, and the emerging light is analyzed by a spectroscope, the hot vapor is found to absorb from the light only those wave lengths which it itself can emit; *i.e.*, those particular wave lengths for which e_λ of the vapor is large are the same wave lengths for which a_λ is also large. This phenomenon is very beautifully illustrated by the Fraunhofer lines in the solar spectrum. These are lacunae in the continuous spectrum reaching us from the sun, which are due to the absorption of particular wave lengths by the relatively cool vapors in the outermost regions of the sun. These wave lengths are the same as would be emitted by these vapors if they were maintained at a sufficiently high temperature.

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[1] PFLUGER, *Ann. Physik*, **7**, 806 (1902).

The discussion of Kirchhoff's law further suggests how a black body may be made in practice. If a small hole were made in the walls of an enclosure, the radiant energy emerging per unit area should be approximately $E_\lambda d\lambda$, which is the same as the emission from a black body, $e_\lambda{}^b d\lambda$. This is only approximately so, however; for, when the hole exists, the condition of equilibrium is violated as energy is being continually lost from the enclosure and the foregoing discussion is not strictly applicable. Practically, this presents no difficulty, for with a suitably shaped enclosure, such as a long cylinder, as much as a quarter of the area of one end may be removed and the radiation is still found to possess very closely the properties of black-body radiation. In such a case the walls of the enclosure should be of a highly absorbing material. The largest possible fraction of any radiation impinging from the outside on the open end of the enclosure must be absorbed before it can again emerge after successive reflections, if the body is to be a good approximation to a perfect black body. For rough absorption measurements, a flat plate painted with soot, or with platinum black or bismuth black, is satisfactory for use as a black body. These substances have very high absorptivities, ranging from 96 to 99 per cent, for those wave lengths which contain appreciable energy in heat radiation.

Before continuing to a discussion of the dependence on temperature of the energy density in an enclosure, it is of interest to see that the thermodynamic theory of heat radiation also predicts the existence of a radiation pressure. If we consider black-body radiation characterized by a temperature T_1 contained in a cavity with perfectly reflecting walls and allow these walls to contract so that the volume decreases by an amount dv, the energy density inside the enclosure must increase. It will be shown in connection with the derivation of Wien's law that this still has the characteristics of black-body radiation, but it is radiation which would be in equilibrium with a black body at a temperature of, say, T_2. Thus, if an absorbing body were present, a temperature difference might be established by the compression of this radiation. As this could be used to obtain work by means of a thermodynamic engine, work must have been expended to establish the temperature difference, and this work can only have been the work done in contracting the walls against the pressure exerted by the radiation; *i.e.*, the work done is equal to $p\,dv$, where p is the pressure exerted by the radiation.

2-4. Stefan's Law.—Let us now consider the variation of the energy density in an enclosure with the temperature of which we have seen it is a function. For simplicity we shall consider that the radiation is contained in a cylinder with perfectly reflecting walls which is closed by a piston whose face is also perfectly reflecting. Let us further assume that there is a small black plug of negligible heat capacity let through the walls as a means of introducing heat into the enclosure. If the energy density in the enclosure in equilibrium with the black plug, which is maintained at a temperature T, is E, and if the volume of the enclosure is v, then the total energy in the enclosure is Ev. If now the piston is allowed to move, increasing the volume by an amount dv, an amount of heat δQ will flow in from the source maintaining the black plug at the temperature T, and the energy density will remain the same, as this depends only on the temperature. An amount of work pdv will be done, where p is the radiation pressure, and the total energy will be increased by an amount $d(Ev)$. We then have by the first law:

$$\delta Q = d(Ev) + pdv$$

or by Eq. (2-4)

$$d\phi = \frac{d(Ev)}{T} + \frac{pdv}{T}$$

Performing the differentiation on the right, and recalling that $p = E/3$, by Eq. (1-25), for this isotropic radiation, we have

$$d\phi = \frac{v}{T}dE + \frac{4E}{3T}dv$$

Since $d\phi$ is a perfect differential we must have $v/T = \partial\phi/\partial E$ and $4E/3T = \partial\phi/\partial v$. Differentiating the first of these equations with respect to v and the second with respect to E, and equating the two values of $\partial^2\phi/\partial E\partial v$, we find

$$\left[\frac{\partial}{\partial v}\left(\frac{v}{T}\right)\right]_E = \left[\frac{\partial}{\partial E}\left(\frac{4E}{3T}\right)\right]_v$$

where the subscripts indicate which variable is held constant. For the left side this means, since E depends only on the temperature, that T does not change with v when E is held constant, so that

$$\frac{1}{T} = \frac{4}{3T} - \frac{4E}{3T^2}\frac{dT}{dE} \quad \text{or} \quad \frac{dE}{E} = \frac{4dT}{T}$$

which on integration gives

$$E = bT^4 \tag{2-11}$$

This is known as Stefan's law, which states that the energy density in black-body radiation is proportional to the fourth power of the absolute temperature with which the radiation is in equilibrium; the constant of proportionality is the integration constant b.

In an experimental demonstration of the truth of this relation, that which is directly measured is the total emissive power of a black body,

πK_b; or the total normal emissive power, K_b. We may find the relation between E and K_b in the following way: Consider a small volume v at the center of a large spherical enclosure with black walls containing temperature radiation. Let us take an element dA of the walls, its linear dimensions being small compared to those of v. The solid angle subtended at dA by v may be broken up into a number of small solid angles, $d\omega = f/r^2$, where f is the area subtended at the center of the sphere of radius r, as in Fig. 2-4. If s is the length of the infinitesimal truncated cone cut from $d\omega$ by v, then the time taken by radiation traveling with a velocity c from dA to pass through v is $dt = s/c$. Hence, by Eq. (2-5), for a black surface integrated over all wave lengths, we have the energy contained in this truncated cone given by $K_b fs\, dA/cr^2$; the cosine term of Eq. (2-6) is equal to unity, as the elementary solid angles leaving dA and passing through v are all approximately normal to the surface. If we sum this expression over the whole solid angle subtended by v at dA we obtain

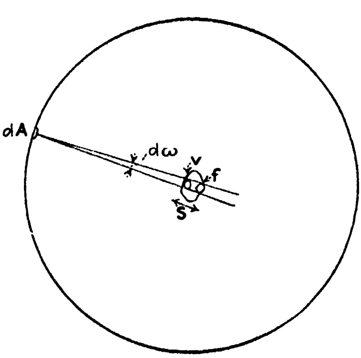

FIG. 2-4.—Illustration of the relation between emissive power and energy density.

$$K_b \frac{dA}{cr^2} \sum fs = K_b \frac{dA}{cr^2} v$$

as the value of the energy originating from dA contained in v. To find the energy content due to all the dA's making up the walls of the sphere, we replace dA by its value in polar coordinates as shown in Fig. 2-2 and integrate over the whole sphere.

$$\begin{aligned} \text{Energy in } v &= \frac{K_b v}{cr^2} \int_0^{2\pi} \int_0^{\pi} r^2 \sin\theta \, d\theta \, d\phi \\ &= \frac{4\pi K_b v}{c} \end{aligned}$$

The energy density in v due to this homogeneous isotropic black-body radiation is this energy divided by v; so we have:

$$E = \frac{4\pi K_b}{c}$$

Substituting this value for E in Eq. (2-11), we obtain

$$\pi K_b = \frac{bc}{4} T^4 \equiv \sigma T^4 \qquad (2\text{-}12)$$

This expression for the total emissive power of a black body in terms of the temperature and Stefan's constant σ, which is written for $bc/4$, is simply a slightly different form of Stefan's law.

The existence of the fourth-power law was first suggested by Stefan[1] in 1879 from a consideration of Tyndall's observations on the radiation from hot platinum wires, and Boltzmann[2] gave the thermodynamic derivation of the law in 1884. Measurements by Lummer and Pringsheim[3] confirmed the correctness of the law to within their experimental error. The measurement of the absolute value of the proportionality constant σ is very difficult, but it has been attempted by a number of investigators. Some of the earliest and most recent determinations of this quantity are given in the following table; the value listed opposite Birge is the one which he considers to be the most probable value. An excellent account of the difficulties connected with these measurements and the various methods of overcoming them is given by Glazebrook in volume IV of the "Dictionary of Applied Physics."

Investigators	Date	σ in ergs · cm.$^{-2}$ sec.$^{-1}$ deg.$^{-4}$
Kurlbaum[4]	1898	5.45×10^{-5}
Shakespear[5]	1912	5.67
Gerlach[6]	1920	5.80
Coblentz[7]	1920	(5.722 ± 0.012)
Hoffmann[8]	1923	(5.764 ± 0.052)
Kussmann[9]	1924	(5.795 ± 0.058)
Hoare[10]	1928	(5.735 ± 0.014)
Birge[11] (probable average)	1929	(5.735 ± 0.011)
Hoare[12]	1932	(5.737 ± 0.017)

It is difficult to determine πK_b, the total emissive power of a black body, though such measurements have been made. In general, however, only a known fraction of this energy is measured. An apparatus to measure such a fraction is shown in Fig. 2-5. B represents the aperture in a cavity which is maintained at various constant temperatures, A_1 the area of a hole in a water-cooled diaphragm, and A_2 the area of a small blackened plate to receive the radiation from B. The sizes and positions of B, A_1, and A_2 must be such that any radiation reaching A_2 through A_1

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[1] Stefan, *Wien. Ber.*, (2), **79**, 391 (1879).

[2] Boltzmann, *Wied. Ann.*, **22**, 31, 291 (1884).

[3] Lummer and Pringsheim, *Ann. Physik*, **63**, 395 (1897); **3**, 159 (1900).

[4] Kurlbaum, *Wied. Ann.*, **65**, 746 (1898).

[5] Shakespear, *Proc. Roy. Soc.*, **86**, 180 (1912).

[6] Gerlach, *Ann. Physik*, **50**, 259 (1916); *Zeits. Physik*, **2**, 76 (1920).

[7] Coblentz, *Bur. Standards Bull.*, **12**, 503 (1916); **15**, 529 (1920); **17**, 7 (1922).

[8] Hoffmann, *Zeits. Physik*, **14**, 301 (1923).

[9] Kussmann, *Zeits. Physik*, **25**, 58 (1924).

[10] Hoare, *Phil. Mag.*, **6**, 828 (1928).

[11] Birge, *Phys. Rev. Suppl.* (*Rev. Mod. Phys.*), **1**, 1 (1929).

[12] Hoare, *Phil. Mag.*, **13**, 380 (1932).

must have come from within the opening B. Thus A_2 is bathed with black-body radiation, apparently coming from A_1, and, hence, A_1 may be considered as the opening in the black body which is supplying the energy. The energy leaving A_1 normally into the solid angle $d\omega$ in unit time is $K_bA_1d\omega$. The solid angle subtended by A_2 at A_1, a distance D away, is A_2/D^2, so the energy Q intercepted per second by A_2 is

$$Q = \frac{K_bA_1A_2}{D^2}$$

Substituting the value for K_b from Eq. (2-12) we find

$$Q = \frac{A_1A_2\sigma T^4}{\pi D^2}$$

Hence, Q is proportional to T^4 and a graph of Q against T^4 should be a straight line if Stefan's law is true. The value of σ may be found from the slope of this line, if the values of the geometrical factors are known, from the relation

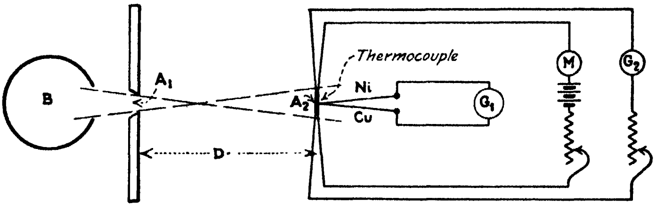

FIG. 2-5.—An apparatus to measure Stefan's constant, by intercepting a known fraction of the radiation from a black body. The energy received by the blackened disk A_2 is measured by a thermocouple which is calibrated by supplying energy to the disk at a known rate from the battery.

$$\sigma = \frac{\pi D^2}{A_1A_2}\frac{dQ}{d(T^4)} \tag{2-13}$$

where $dQ/d(T^4)$ is the slope.

In the early determinations the black body, whose opening is B, was a copper or iron vessel, blackened on the inside, and heated by immersion in constant-temperature baths or by an enclosing gas furnace. In later work it has generally consisted of a porcelain or quartz tube, closed at one end, and heated by an electric current passing through a coil of wire wound around it. The temperature of this furnace is measured with a thermocouple. The heat input per second to the blackened-disk receiver may be determined by allowing it to come to an equilibrium temperature when irradiated by the black body; a thermocouple behind the disk receives the radiation from its back surface. The e.m.f. developed by the thermocouple is then a measure of the temperature of the disk, and this can be reduced to an absolute measure of the heat input to the disk by electrically heating it and noting the energy input necessary to produce the same e.m.f. when the shutter in front of the black body is closed. The blackened disk may alternatively contain the thermocouple elements buried in it, or it may be located in one arm of a Wheatstone bridge, so that its change in resistance is a measure of the temperature. Numerous corrections have to be applied, if great precision is attempted, to allow for the incomplete "blackness" of the radiator and receiver, atmospheric absorption, radiation from the shutter and walls, heat losses by the receiver due to conduction through the air and supports, etc.

2-5. Experiment on Stefan's Law.—The following simple method, without applying any of the elaborate corrections which have just been mentioned, is quite adequate to show that the total emissive power of a black body is proportional to the fourth power of the absolute temperature and to give a value for Stefan's constant σ, at least correct in order of magnitude.

The black body may be constructed from a quartz tube $\frac{1}{2}$ in. in diameter and 5 or 6 in. long whose outside is wound with a long thin platinum strip through which the heating current flows, and this is in turn surrounded by asbestos wrappings. One junction of a thermocouple whose elements are capable of withstanding a high temperature is introduced into the center of the tube from one end; the wires should pass through quartz capillary tubes for insulation and mechanical protection. The junction inside the large quartz tube is packed about with asbestos wool to supply a back to the black body which is at the same temperature as the junction. The wires of the other junction are connected to copper leads and these connections are immersed in a constant-temperature bath, such as one containing ice and water. The calibration of the thermocouple must be performed by an auxiliary experiment with a series of known temperatures, such as metallic melting points; or, if the elements are of some standard composition, such as platinum and 90 per cent platinum–10 per cent rhodium, the calibration may be obtained from the manufacturers.

A still simpler source of temperature radiation, which is about as satisfactory for the present purpose, is made by bending a thin sheet of platinum into the form of a semicylinder about 6 or 8 cm. in length and 0.5 cm. in diameter. The cylinder is supported by the metal rods which form its ends as shown in Fig. 2-6, and the inside is blackened by applying to it a thick coating of varnish heavily impregnated with black manganese or chromium oxide. This cylinder is heated by passing a moderately heavy current through it lengthwise. The platinum should be surrounded by a cylindrical asbestos shield, about 1 cm. in radius, which contains, opposite the center of the opening of the semicylinder, a slit about 1 cm. long and 2 or 3 mm. wide. The shield assists in maintaining the platinum at a high temperature, and sufficient radiation emerges from the slit for use in this and the following experiment. Two platinum wires are fastened to the outer wall of the cylinder (by tapping them to it with a small hammer in the flame of a blow torch) at approximately its center, opposite the opening, and about 1 cm. apart along its length. These wires lead to a Kelvin double bridge which thus measures the resistance of this portion of the cylinder. From the value of this resistance, which is measured for the various heating currents passed through the cylinder, the temperature can be calculated by means of the empirical relation for platinum:[1]

$$R_{T'} = R_0(1 + (3.981 \times 10^{-3})T' - (5.85 \times 10^{-7})T'^2)$$

where R_0 is the resistance at 0°C. and $R_{T'}$ the resistance at T'°C. R_0 may be found by immersing the platinum strip in an ice bath and measuring its resistance with as small a current flowing through it as possible. It is most convenient to plot a graph of $R_{T'}/R_0$ against T' in degrees centigrade from the above relation and from this the absolute temperature T of the strip can be found for any observed resistance by adding 273.2° to the corresponding value of T'.

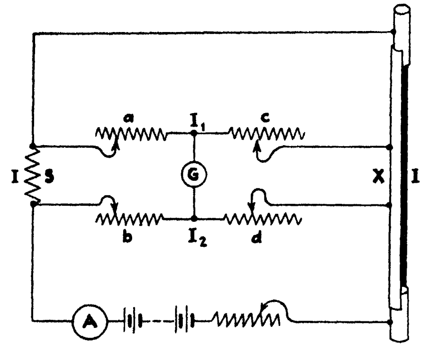

Fig. 2-6.—Experimental realization of an approximately black body in the form of an electrically heated semicylinder of platinum. The temperature is determined from the resistance, which is measured with a Kelvin double bridge.

The details of the Kelvin bridge, which is designed to make accurate measurements of low resistances, are also shown in Fig. 2-6. X is the resistance of the strip which is to be measured, and S is a known resistance which is of the same order of magnitude as X and which is designed to carry the same heavy current. The resistances a, b, c, and d are higher, variable resistances. When the bridge is in balance there is no potential difference across the terminals of the galvanometer. In this condition the current through c and a is, say, I_1; that through b and d, I_2; and that through X and S, I. The condition for balance is then $cI_1 = dI_2$, and $aI_1 = bI_2$, so by division we have $c/a = d/b$. We also have $cI_1 = XI + dI_2$, and $aI_1 = SI + bI_2$, so solving for SI and XI, and taking the ratio, we find

$$\frac{X}{S} = \frac{c}{a} = \frac{d}{b}$$

In some forms of this instrument, a is equal to c, and b is equal to d; all four are fixed and the balance is obtained by varying S. In the Wolff pattern, S is fixed, c and d may be made 100, 50, or 25 ohms each and are kept equal; a and b are variable over a wide range and necessarily remain equal by the way in which the dial switches are wired. The Kelvin bridge is greatly superior to the ordinary form of the Wheatstone bridge for the measurement of low resistances because of the absence of lead-wire corrections. The small unknown resistances of the lead wires to the center taps on the platinum strip are negligible in comparison with the resistances c and d, and there are no lead wire errors in the branch containing the unknown resistance.

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[1] "International Critical Tables," vol. 6, p. 136, McGraw-Hill (1929).

A water-cooled diaphragm may be made from two parallel copper sheets 15 or 20 cm. square, separated about 0.5 cm. by a small brass block at the center and by brass rods along the edges, all these joints being soldered. A hole tapering from 0.3 to 0.2 cm. may be made in the central block for the passage of the radiation, and a heavy metal shutter arranged so that it may be slid over this hole when it is desired to shut off the radiation. This diaphragm should be placed as closely in front of the black body as possible to facilitate the fulfillment of the geometrical conditions discussed in connection with Fig. 2-5, for the emitting area of the black body, as limited by the slit in the asbestos shield, is not large.

The receiver may be in the form of a thin disk about 0.5 cm. in diameter and should be made from a material of fairly high electrical resistance, such as nickel, nichrome, or manganin. The sharp angles of two hairpins of rather fine copper wire are soldered to the disk at the opposite ends of a diameter. These are waxed to a framework of glass, and both support the disk and serve in its calibration. The thermocouple wires, which may conveniently be made of nickel and copper, should also be rather fine. The ends are twisted together for a very short distance, a fraction of a millimeter, and this junction is soldered to the center of the back of the disk. As small an amount of solder as possible should be used in making these connections. The thermocouple wires must actually be in contact or there will be an undesired difference in potential between their ends when the heating current is flowing in the disk. The front surface of the disk may be blackened by coating it lightly with very thin varnish and holding it a little distance above a lump of burning camphor so that the surface becomes covered with soot. The surface may be rendered still more highly absorbing by covering it with a deposit of platinum black or bismuth black.

The receiving element and its supporting framework should be mounted inside a water-jacketed calorimeter can, the open end of which is next to the diaphragm in order that the surrounding temperature may be kept constant. The junctions of the thermocouple wires with heavier copper leads may be waxed to a spring, on the supporting framework, which presses the junctions against the inside of the can so that these also may be kept at a constant temperature. These copper leads, which may be of any convenient length, then go to a galvanometer of high voltage sensitivity, whose calibration need not be known. One of the top and one of the bottom supporting wires are connected in series with a battery of about 6 volts, a rheostat, and a milliammeter M. The remaining pair of wires are connected through a resistance box R of several thousand ohms and a galvanometer of moderate current sensitivity. The sensitivity of this galvanometer G_2 must be known or found from an auxiliary experiment, for it is used to determine the potential drop across the disk when the calibrating current is flowing from the battery. These electrical connections are shown in Fig. 2-5. In adjusting the apparatus, the receiving disk should be as close to the opening in the diaphragm as possible, consistent with the geometrical condition that all the radiation reaching the disk from the opening comes from the interior of the black body.

Readings of the thermocouple galvanometer deflections are taken with the shutter open and closed at a series of temperatures of the black body. These deflections are then plotted against the fourth power of the absolute temperature of the black body as determined from the resistance of the platinum strip by means of the Kelvin bridge. It is then necessary to determine the relation between the deflection of the galvanometer and the energy received by the disk. To determine this relation the shutter is closed and the deflections of both galvanometers are observed for various values of the heating current sent through the receiving disk by the battery. The potential drop across the disk is computed by multiplying the current through the galvanometer G_2 (obtained from the deflection and the known sensitivity) by the total external resistance in the circuit, which may be taken as the sum of the galvanometer resistance and that of the resistance box, for the resistance of the leads and of the disk is in general negligible. The rate of input of electrical energy in watts may then be plotted against the equilibrium deflections of the thermocouple galvanometer G_1. From this graph the curve of the thermocouple-galvanometer deflection against T^4 may be plotted as watts input to the disk against T^4. This last curve should be approximately a straight line, which constitutes a verification of Stefan's law. The value of the slope of this line, together with the area of the hole in the diaphragm, the area of the receiving disk, and their distance apart, permits the calculation of the constant σ from Eq. (2-13).

2-6. Wien's Laws.—In addition to accounting for the variation of the total emissive power of a black body with temperature, as expressed by Stefan's law, thermodynamics can go still further and predict, to some extent, the energy distribution among the wave lengths present in black-body radiation. This extension of the theory of radiation was made by Wien[1] in 1893.

As a preliminary step in this discussion it is necessary to show that if the radiation in an enclosure undergoes an adiabatic change it maintains the spectral energy-distribution characteristic of a black body throughout the process. By an adiabatic change is meant one during which there is no exchange of heat between the radiation and its surroundings. Let us consider a cylinder closed by a piston, all of the internal surfaces being perfectly reflecting. This cylinder contains radiation which would be in equilibrium with a black body at a temperature T_1. If the piston moves outward, the volume increases and the energy density decreases. It is conceivable that the energy distribution over the wave lengths comprising the radiation is not that characteristic of a black body at any temperature whatever. If this is true we may introduce into the enclosure a very small black body of negligible heat capacity, and the spectral energy distribution will then become that characteristic of a black body at some temperature, say T_2. Such a process is not a reversible one, however; for, if the black body were removed, the radiation would still be that characteristic of the black body. With this small black body still remaining in the enclosure the piston is returned to its original position. The work done by the radiation during the expansion, $\int pdv$, is the same as the work done on the radiation during the compression, for the total energy density, which determines the pressure, must have been the same at corresponding stages for both processes. If one part of a process is irreversible, the original state cannot be reestablished without the expenditure of external work, for a loss of available energy has occurred at that point in the process. But in our instance the original state has been reestablished with no expenditure of external work, hence the hypothetical irreversible process of the redistribution of energy over the wave lengths cannot have occurred. The energy distribution must have remained that characteristic of a black body during this adiabatic process.

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[1] WIEN, *Preuss. Akad. Wissens. Sitz. Ber.*, p. 55 (1893).

With this assurance let us investigate how the characteristic temperature and energy density of the radiation change if we adiabatically increase the volume occupied by the radiation. The container for the radiation we may now imagine to be spherical in shape, with perfectly reflecting elastic walls, and we shall assume that the increase in volume arises from an elongation of the radius r. Since there is no transfer of heat through these perfectly reflecting walls we may write the equation for the first law as

$$0 = d(Ev) + pdv$$

Since $p = E/3$ for isotropic radiation, this may be integrated immediately to give

$$v^4E^3 = v'^4E'^3 \tag{2-14}$$

where v, v', E, and E' represent the volumes and energy densities before and after the change. But by Stefan's law, E is proportional to T^4, so Eq. (2-14) becomes

$$vT^3 = v'T'^3 \tag{2-15}$$

Since the volume is proportional to r^3, we may also write

$$rT = r'T' \tag{2-16}$$

We saw, when considering the pressure exerted by light, that if a beam of radiation of wave length λ is incident normally upon the surface of a mirror moving toward it with a velocity u, the ratio of the wave lengths in the reflected and incident beams is given by Eq. (1-21) as

$$\frac{\lambda'}{\lambda} = \frac{c - u}{c + u}$$

If the mirror is moving away from the source of light, the sign of the velocity u is changed and we obtain for the ratio of the reflected and incident wave lengths,

$$\frac{\lambda'}{\lambda} = \frac{c + u}{c - u} \quad \text{or} \quad \frac{\lambda'}{\lambda} = 1 + \frac{2u}{c},$$

if we expand this expression and neglect second and higher powers of the small quantity u/c. Hence the change in wave length at such a reflection is

$$d\lambda = \lambda' - \lambda = \frac{2\lambda}{c}u$$

For oblique incidence, at an angle θ with the normal to the mirror, the effective velocity of the mirror is that which is normal to the wave front, or $u \cos \theta$, so that

$$d\lambda = \frac{2\lambda}{c}u \cos \theta \tag{2-17}$$

We may now apply these ideas to the radiation in the spherical enclosure. The length of each chord traversed by a ray between reflections is $2r \cos \theta$, as may be seen from Fig. 2-7. Hence the time dt between reflections is given by

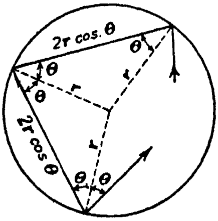

FIG. 2-7.—The path of a ray in a spherical enclosure with perfect specularly reflecting walls.

$$dt = \frac{2r \cos \theta}{c} \tag{2-18}$$

Hence the rate at which the wave length changes with the time, which is given by the change in wave length at a reflection divided by the time between reflections, is

$$\frac{d\lambda}{dt} = \frac{2\lambda u \cos \theta}{c} \frac{c}{2r \cos \theta} = \frac{u\lambda}{r}$$

Writing dr/dt for u, we obtain

$$\frac{d\lambda}{dt} = \frac{dr}{dt}\frac{\lambda}{r} \quad \text{or} \quad \frac{d\lambda}{\lambda} = \frac{dr}{r}$$

This equation may be integrated directly, yielding

$$\frac{\lambda}{r} = \frac{\lambda'}{r'} \tag{2-19}$$

Combining this with Eq. (2-16), we find

$$\lambda T = \lambda' T' \tag{2-20}$$

This is Wien's *wave length-temperature displacement law,* which tells us that if black-body radiation corresponding to a temperature T_1 is altered by an adiabatic process to that corresponding to some other temperature T_2, a wave length λ_1 of the original radiation at T_1 corresponds to a wave length λ_2 in the radiation at T_2 through the relation $\lambda_1 T_1 = \lambda_2 T_2$.

We shall now investigate how the energy density in some particular wave-length range is altered by an adiabatic change in volume. Since the volume is proportional to r^3, Eq. (2-14) may be written

$$r^4 E = r'^4 E' \tag{2-21}$$

But if the container, when we developed this expression, had been filled not with all the wave lengths emitted by a black body but with only a monochromatic range between λ and $\lambda + d\lambda$, we should have obtained the same equation with the substitution of the monochromatic energy density $E_\lambda\, d\lambda$, in place of the total energy density E. Thus

$$r^4 E_\lambda\, d\lambda = r'^4 E_{\lambda'}\, d\lambda' \tag{2-22}$$

Now if Eq. (2-19) is true for any given wave length, it is also true for a slightly different one; *i.e.*,

$$\frac{\lambda + d\lambda}{r} = \frac{\lambda' + d\lambda'}{r'}$$

and subtracting Eq. (2-19) from this, we obtain

$$\frac{d\lambda}{r} = \frac{d\lambda'}{r'} \tag{2-23}$$

Hence Eq. (2-22) may be written

$$r^5 E_\lambda = r'^5 E_{\lambda'}$$

and by the use of Eq. (2-16) this may be changed to

$$\frac{E_\lambda}{T^5} = \frac{E_{\lambda'}}{T'^5} \tag{2-24}$$

This is Wien's *energy-temperature displacement law,* which shows that the energy density in a narrow wave-length range $d\lambda$, when divided by the fifth power of the temperature, is equal to the energy density in the corresponding wave-length range after an adiabatic change when this is divided by the fifth power of the final temperature. Or, if this relation is taken in conjunction with Wien's first law, namely, that $\lambda T = \lambda' T'$, we may say that, if we consider a particular wave length λ and its energy density E_λ at a particular temperature T and then change to a different temperature T', Wien's first law defines a corresponding wave length λ' at this temperature and Eq. (2-24) gives the energy density in this corresponding wave length. The significance of the term "corresponding" is perhaps clearer if the first chosen λ is one endowed with some outstanding characteristic, say it is that particular λ at which E_λ is a maximum for the temperature T, if such a maximum value for E_λ exists. Then Wien's two laws give the wave length λ' which, at the new temperature T', contains the maximum energy density, and give also the value of this energy density in terms of E_λ, T, and T'.

An even more interesting point may be brought out by the following considerations. Choose any numerical value x_1 for the product λT. Then for any value λ_1 there will be a T_1, such that $\lambda_1 T_1 = x_1$ and $E_{\lambda_1}/T_1{}^5$ will then equal some number, say y_1. Take another value of λ, say λ_2, and there will be some temperature T_2 such that $\lambda_2 T_2 = x_1$ again, and $E_{\lambda_2}/T_2{}^5$ still equals y_1 because of Eq. (2-24). Thus an infinite number of different λ's are associated with an equal number of T's in such a way that the corresponding energy density at each wave length divided by the corresponding T^5 always gives the same numerical value y_1. Now choose a greater value for λT, say x_2. Again we find that for all possible λ's and T's whose products are equal to x_2, the ratio E_λ/T^5 is but one number y_2. Continuing in this way, we find that for any value of $x = \lambda T$ there is but a single corresponding value $y = E_\lambda/T^5$. So if we plot $x = \lambda T$ against $y = E_\lambda/T^5$ we obtain a single curve which describes the dependence of the energy density on the wave length for all temperatures.

If the plot of x against y gives a single curve, then obviously y is some function of x; *i.e.*,

$$\frac{E_\lambda}{T^5} = f(\lambda T) \qquad (2\text{-}25)$$

or by Eq. (2-20)

$$E_\lambda \lambda^5 = \phi(\lambda T) \qquad (2\text{-}26)$$

This is all that thermodynamics can tell us in regard to the dependence on temperature of the energy density in a particular wave-length region. The analytical form of the function f or ϕ of the product λT is entirely unknown and unpredictable, unless special additional assumptions are made. These expressions may, of course, be written in terms of the monochromatic emissive power instead of the energy density, by means of the relation between these quantities developed in connection with Stefan's law. It is this monochromatic emissive power which is observed in any experiment.

The implications of Wien's two laws have been amply verified by experiment. It has been found that $\lambda_{\max} T$ is a constant well within experimental error over a large range of temperatures, $\lambda_{\max}$ being the wave length for which the black-body monochromatic emissive power is a maximum. It has also been shown that $E'_{\max} T^{-5}$ is a constant, where $E'_{\max}$ is a measured quantity that is proportional to the maximum monochromatic energy density or emissive power. In addition, $E' T^{-5}$ plotted against λT gives a single curve as the theory demands. Figure 2-11 shows the curves representing the energy distribution over the spectrum of black-body radiation for a series of temperatures. The hatched areas are irregularities caused by selective absorption of the radiation in passing through the surrounding medium. If the abscissas of these curves are each multiplied by the appropriate temperature and the ordinates are divided by these temperatures raised to the fifth power, the curves are superposed on one another as in Fig. 2-12. It is the function of the product λT determined by these curves which we shall endeavor to find upon some additional assumption.

2-7. Wien's Hypothesis.—Wien,[1] in 1896, endeavored to arrive at a definite form of the function $f(\lambda T)$ by making some very special assumptions as to the mechanism of emission and absorption of radiation by a black body. He assumed that the radiation was produced by an oscillator of atomic dimensions, that the frequency of the emitted wave was proportional to the kinetic energy of the oscillator, and that the intensity in any particular wave-length range was proportional to the number of oscillators which had the requisite energy. On these rather reasonable but arbitrary assumptions he deduced the following energy-distribution law:

$$E_\lambda d\lambda = \frac{A}{\lambda^5} e^{-c_2/\lambda T} d\lambda \tag{2-27}$$

where A and c_2 are constants. A plot of this function fits the experimental curves quite well at short wave lengths (from 1 to 3μ, where $\mu = 10^{-4}$ cm. $= 10^4$ Ångströms), but it predicts consistently too small an energy at longer wave lengths, as may be seen by an examination of the curves obtained by experimental investigators to whom references will be given a little later. In view of the arbitrary nature of the assumptions involved, this law has never been considered to have a very firm theoretical foundation. However, the exponential form of the function of the product λT is so satisfactory at short wave lengths that any successful radiation law must reduce approximately to such an exponential function in this region of the spectrum.

2-8. Rayleigh-Jeans Hypothesis.—An expression of much greater significance was developed by Rayleigh,[2] in 1900, and later shown by Jeans[3] to be a necessary consequence of classical dynamics and statistics.

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[1] WIEN, *Ann. Physik*, **58**, 662 (1896).

[2] RAYLEIGH, *Phil. Mag.*, **49**, 539 (1900).

[3] JEANS, *Phil. Mag.*, **17**, 229, 773 (1909); **18**, 209 (1909).

Without making special assumptions, as occur in Wien's hypothesis, this theory applies the classical statistical principle of the equipartition of energy, which has been well verified in many physical phenomena, to the case of radiation. There was every expectation that it should lead to the correct result in this instance. As it is based on such apparently solid foundations, it is worth while considering briefly, though it makes a prediction flatly contradicted by experiment.

Let us examine the possible number of different wave lengths that can exist in a steady state of continuous vibration in an enclosure containing a medium capable of supporting these vibrations. The condition for this steady state of vibration is that there shall be standing waves formed by reflection at the walls, and for this to occur it is necessary that the path length from wall to wall, in any particular direction, must be some integral multiple of a half wave length. For simplicity, though the restriction is not necessary, let us assume that the enclosure is a cube of length b on a side. Consider a set of standing waves whose nodal planes are perpendicular to one side of the cube, the normals to these nodal planes making angles θ_1 and θ_2 with the normals from two adjacent walls, as shown in Fig. 2-8. The wave length must then be such that the distances between these nodal planes, along the normals to the walls, are integral fractions of the length of an edge of the cube, *i.e.*,

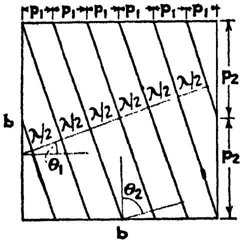

FIG. 2-8.—Section through the nodal planes of a standing-wave system in a cube.

$$p_1 = \frac{\lambda}{2\cos\theta_1} = \frac{b}{n_1}$$

$$p_2 = \frac{\lambda}{2\cos\theta_2} = \frac{b}{n_2}$$

where n_1 and n_2 are integers. Similarly, if these nodal planes had been located obliquely in the cube a three-dimensional consideration would have shown that we must have the following three conditions fulfilled, where θ_1, θ_2, and θ_3 are the angles between the normals to the nodal planes and the normals to the walls, and n_1, n_2, and n_3 are any integers:

$$\begin{aligned} n_1 &= \frac{2b}{\lambda}\cos\theta_1 \\ n_2 &= \frac{2b}{\lambda}\cos\theta_2 \\ n_3 &= \frac{2b}{\lambda}\cos\theta_3 \end{aligned} \tag{2-28}$$

If we square these equations and add them together, remembering that the sum of the squares of the direction cosines is equal to unity, we have

$$n_1^2 + n_2^2 + n_3^2 = \left(\frac{2b}{\lambda}\right)^2 = \left(\frac{2b\nu}{c}\right)^2 \qquad (2\text{-}29)$$

since $c = \lambda\nu$ where ν is the frequency of the wave and c is its velocity of propagation. But this is the equation of a sphere drawn in a frame of reference with coordinates n_1, n_2, and n_3, with its center at the origin of coordinates and a radius equal to $2b\nu/c$. In the positive octant of this sphere all the n's are positive integers, corresponding to the requirements of Eqs. (2-28), so that the values of the wave length or frequency satisfying these three equations may be found from those triads of n's contained in the positive octant of this sphere; *i.e.*, the number of different standing waves possible in this cube, with frequencies between $\nu = 0$ and $\nu = \nu$, is

$$N = \frac{1}{8}\frac{4}{3}\pi\left(\frac{2b\nu}{c}\right)^3 = \frac{4}{3}\pi b^3\left(\frac{\nu}{c}\right)^3 \qquad (2\text{-}30)$$

and the number of different standing waves per unit volume with frequencies between ν and $\nu + d\nu$ is given by the differential of this expression, divided by b^3, or

$$dN = \frac{4\pi\nu^2}{c^3}d\nu$$

Here it has been assumed that the velocity of propagation of these waves is independent of the frequency. There is one further point that has not been considered in counting the number of different standing waves in this frequency range, and that is the polarization. We may consider a particular standing-wave system due to a frequency ν as made up of a large number of waves with their electric force or displacement vectors arbitrarily oriented in a plane perpendicular to the wave normal; or we may alternatively conceive of this wave system as being composed of two waves, with appropriate amplitudes, whose electric vectors are perpendicular to one another and to the direction of propagation, by simply resolving the electric vectors in the original waves along these two mutually perpendicular directions. Thus there are really two waves for each wave system that we have considered, and the total number of standing waves per unit volume with frequencies between ν and $\nu + d\nu$ in the enclosure is given by

$$dN = \frac{8\pi\nu^2}{c^3}d\nu \qquad (2\text{-}31)$$

So far the only arguments involved are those known to be valid for the vibrations of organ pipes, strings, electric waves on wires, etc.

Let us now make use of a theorem of classical statistical mechanics, known as the theorem of equipartition of energy. As will be shown in a subsequent chapter, it is possible to demonstrate that if a very large number of atomic systems, obeying the laws of classical dynamics and with energies involving only quadratic terms in the variables necessary to specify their states, are in thermal equilibrium with one another, then the average energy associated with each variable is the same for each system and is equal to $\frac{1}{2}kT$, where k is the Boltzmann gas constant and T is the absolute temperature. Let us suppose that radiant energy represents the vibration of some sort of a dynamical system, such as an "ether" or a set of atomic electric oscillators. The energy associated with each wave or with each oscillator is $E = \frac{p^2}{2m} + \frac{a}{2}q^2$, where p is the momentum and q is the coordinate representing the displacement, as may be seen by integrating Eq. (1-12) when y is put equal to q and $m(dy/dt)$ is put equal to p. This energy involves only quadratic terms in p and q, hence in the condition of thermal equilibrium each oscillator has an amount of energy equal to $\frac{1}{2}kT$ associated with q and a similar amount associated with p, or the average energy associated with each oscillator or wave is kT. Each different frequency in the enclosure corresponds to a separate wave or oscillator, so the energy per unit volume or the energy density in the enclosure within the frequency range from ν to $\nu + d\nu$ is equal to Eq. (2-31) multiplied by kT, or

$$E_\nu d\nu = \frac{8\pi\nu^2}{c^3} kTd\nu \tag{2-32}$$

or, in terms of λ,

$$E_\lambda d\lambda = \frac{8\pi k}{\lambda^5}(\lambda T)\,d\lambda \tag{2-33}$$

since $\nu = c/\lambda$, $d\nu = (-c/\lambda^2)\,d\lambda$, and $E_\nu d\nu = -E_\lambda d\lambda$.

These are alternative expressions for the Rayleigh-Jeans law for the distribution of energy with frequency or wave length for black-body radiation. It is observed that it agrees with the requirements of Wien's two laws, since $E_\lambda d\lambda$ is seen to be a function of the product λT. It gives a value for E_λ in agreement with experiment for large values of λ; but as λ becomes small, E becomes increasingly large, which is quite contrary to the facts. Furthermore, if it is integrated over all possible wave lengths from zero to infinity, the total energy is seen to be infinite, which is obviously absurd. Hence this expression is unsatisfactory as a description of the energy distribution in black-body radiation, but it does agree well with the experimental results over the long wave-length range and is thus in a sense complementary to Wien's expression. Any satisfactory radiation law must, for both theoretical and experimental reasons, reduce approximately to this form for sufficiently great wave lengths.

2-9. Planck's Hypothesis.—This highly unsatisfactory state of affairs was terminated in 1901 by Planck,[1] but at the expense of introducing an assumption that ran quite counter to all previous ideas as to the mechanism and absorption of radiant energy by matter. He assumed, essentially, that radiation is not emitted and absorbed in a continuous process but in discrete finite amounts known as quanta, the energy content of each being proportional to the frequency of the radiation; *i.e.*, $\epsilon = h\nu$, where ϵ is the energy of the quantum, ν its frequency, and h is a universal constant known as Planck's constant. Historically there was at first considerable confusion as to whether this "quantizing" should be ascribed to an assumed ability of radiant energy to exist only in quanta, or whether it should be assumed that the atomic oscillators could contain only an integral multiple of these quanta, or whether it was only in the process of emission and absorption that the atom was required to deal in quanta. With the advent of Bohr's atomic theory it became evident that radiant energy is emitted, exists, and is absorbed in quanta because the possible energy content of an atom is limited to certain discrete values, the process of emission or absorption occurring when the atom changes from one energy state to another. On this assumption of discrete quantities of energy, Planck obtained the following expression for the energy density in black-body radiation contained in the frequency range from ν to $\nu + d\nu$:

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[1] PLANCK, *Verh. Deut. Physik. Ges.*, **2**, 237 (1900); *Ann. Physik.*, **4**, 553 (1901).

$$E_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} d\nu \tag{2-34}$$

or in terms of wave lengths

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{\frac{hc}{k\lambda T}} - 1} d\lambda \tag{2-35}$$

This is the most satisfactory radiation law that has been proposed, and it agrees very well with the experimental data over a very large range of wave lengths and temperatures. When λ is small, the exponential term is large in comparison with unity, so that the 1 in the denominator may be neglected and the expression becomes identical with Wien's law. When λ is large, the exponential term is small and we may expand it in terms of $hc/k\lambda T$ retaining only the first power in this quantity and obtain the Rayleigh-Jeans law. Hence this expression fulfills these two conditions which we saw were necessary for a satisfactory radiation distribution law.

We shall not follow Planck's original deduction of this distribution law, but we shall derive it by a method due to Einstein,[1] which introduces several concepts that will be of use in later developments. Let us consider that the walls of the cavity, with which we were dealing earlier in the chapter, are composed of atomic or molecular systems capable of emitting and absorbing radiation. Let us assume that there are only certain stable states or configurations in which an atomic system can exist and that these states are characterized by the energy content of the atom.

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[1] Einstein, *Verh. Deut. Physik. Ges.*, **18**, 318 (1916); *Physik. Zeits.*, **18**, 121 (1917).

If two of these stable states are characterized by the two letters m and n we shall assume that the energy contents of the atoms in these two states are given by ϵ_m and ϵ_n, where we consider that ϵ_m is the greater. We further designate by N_m and N_n the numbers of atomic systems in these two energy states. If the atoms in the state m are capable of spontaneously changing over to the state n, the excess energy being radiated away as a quantum of frequency ν, then the number of atoms which perform this transition in a unit time is proportional to the number of atoms in the state m. The number of atoms undergoing this process is given by

$$A_{m\rightarrow n} N_m$$

where $A_{m\rightarrow n}$ is the probability of this transition occurring. We assume that light of the appropriate frequency ν possesses a catalytic or trigger action capable of stimulating this particular transition. Light in a narrow frequency band $d\nu$ is supposed to possess this property, and all other frequencies outside this range are ineffective in this particular transition. The number of atoms undergoing this stimulated transition per unit time is taken as proportional to the energy density in this frequency region and to the number of atoms in the state m. Hence the number of atoms which are stimulated to change from state m to state n is

$$B_{m\rightarrow n} N_m E_\nu \, d\nu$$

where $B_{m\rightarrow n}$ is the probability of this type of transition. The third type of process which we postulate is that by which atoms are raised from the state n to the state m by the absorption of energy from the radiation striking them. Again we suppose that only this narrow range of frequencies is effective and that the number of atoms leaving state n for state m due to the absorption of this radiation is proportional to the energy density in this frequency range and to the number of atoms in the state n. Hence the number of atoms undergoing this transition is given by

$$B_{n\rightarrow m} N_n E_\nu \, d\nu$$

where $B_{n\rightarrow m}$ is the probability of this type of transition. Now, if we may assume the principle of detailed balancing, in equilibrium as many atoms must change from state m to state n as undergo the reverse transition. Hence we may write

$$N_m(A_{m\rightarrow n} + B_{m\rightarrow n} E_\nu \, d\nu) = N_n B_{n\rightarrow m} E_\nu \, d\nu \qquad (2\text{-}36)$$

We now have to assume the applicability of the classical distribution law to these atomic oscillators. This law states that if a large number of systems obeying the classical statistics are in thermodynamic equilibrium with one another, the number of these systems, each possessing an energy ϵ_i, is given by

$$a_i e^{-\frac{\epsilon_i}{kT}}$$

where a_i is a constant which may contain the a priori probability of the particular energy state, and k and T have their usual significance. Applying this to the atomic oscillators, we have

$$\frac{N_m}{N_n} = \frac{a_m}{a_n} e^{-\frac{(\epsilon_m - \epsilon_n)}{kT}}$$

Putting this for the ratio of N_m to N_n in Eq. (2-36) and writing it explicitly in terms of $E_\nu d\nu$, we obtain

$$E_\nu d\nu = \frac{A_{m\to n}}{B_{n\to m}\frac{a_n}{a_m} e^{\frac{(\epsilon_m - \epsilon_n)}{kT}} - B_{m\to n}} \tag{2-37}$$

As may be seen from the Rayleigh-Jeans law, which is known to give accurate results for long wave lengths, the energy density in a wave-length region becomes infinite when T becomes infinite. For this to be so for Eq. (2-37) we must have

$$B_{n\to m} a_n = B_{m\to n} a_m$$

Hence we may write Eq. (2-37) as

$$E_\nu d\nu = \frac{A_{m\to n}/B_{m\to n}}{e^{\frac{(\epsilon_m - \epsilon_n)}{kT}} - 1} \tag{2-38}$$

Now Wien's displacement laws gave us the relation [*cf.* Eq. (2-26)]

$$E_\lambda d\lambda = \lambda^{-5}\phi(\lambda T) d\lambda$$

or in terms of frequencies

$$E_\nu d\nu = \nu^3 F\left(\frac{T}{\nu}\right) d\nu$$

Hence $(\epsilon_m - \epsilon_n)$ must be proportional to ν, and if we take h as this constant of proportionality, we may write $(\epsilon_m - \epsilon_n) = h\nu$. Also Eq. (2-38) must reduce to the Rayleigh-Jeans form when ν is small, so expanding the exponential term and keeping only the first power in the exponent, and equating the result to Eq. (2-32), we have:

$$\frac{A_{m\to n}}{B_{m\to n}} \frac{kT}{h\nu} = \frac{8\pi\nu^2 kT}{c^3} d\nu$$

Substituting the value of $A_{m\to n}/B_{m\to n}$ obtained from this relation in Eq. (2-38) we obtain Eq. (2-34):

$$E_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} d\nu$$

Thus we have succeeded in deriving the Planck distribution law on the series of assumptions which have been introduced as they became necessary in the development.

There is a third method of deriving Planck's law due to Bose.[1] This derivation is based on the conception of quanta of radiant energy or photons as particles which obey a particular type of statistics known as the Bose-Einstein statistics. Bose showed on this basis that the average energy of a photon with a frequency ν in black-body radiation is equal to

$$\frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

If this expression is true, Planck's law follows immediately from Eq. (2-31) on multiplication by the above factor. In this derivation the equilibrium is conceived of as an equilibrium between the photons themselves; the atomic radiating systems act merely as mechanisms for the transference of energy from one frequency range to another. An interesting summation of the present state of the light quantum hypothesis and of the various assumptions involved in the theoretical treatments of radiation has been given by Jordan.[2]

The maximum value of E_λ, according to Planck's equation, occurs at that value of λ for which

$$\lambda^5\left(e^{\frac{hc}{k\lambda T}} - 1\right)$$

in Eq. (2-35) is a minimum. Differentiating this with respect to λ and equating the result to zero, we find

$$e^x - 1 = \frac{x}{5}e^x, \text{ where } x = \frac{hc}{k\lambda T}$$

The approximate solution of this equation is $x = 4.9651$, therefore

$$\lambda_{\max} T = \frac{hc}{k\,4.9651} \tag{2-39}$$

Hence Planck's constant h may be found from a knowledge of the velocity of light, the Boltzmann gas constant, and the value of $\lambda_{\max} T$. If we integrate Eq. (2-34) over all values of ν from zero to infinity, we obtain an expression which we may equate to the total energy density as given by Stefan's law. Writing z for $h\nu/kT$ in Eq. (2-34) and integrating, we obtain

$$\begin{aligned} E &= \frac{8\pi k^4T^4}{h^3c^3}\int_0^\infty \frac{z^3}{e^z - 1}dz \\ &= \frac{8\pi k^4T^4}{h^3c^3}\int_0^\infty z^3(e^{-z} + e^{-2z} + e^{-3z} + \cdots)dz \end{aligned}$$

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[1] **Bose**, *Zeits. Physik*, **26**, 178 (1924).

[2] **Jordan**, *Ergeb. Exakt. Naturwiss.*, **7**, 158 (1928).

$$E = \frac{48\pi^5 k^4 T^4}{90 c^3 h^3}$$

since

$$\int_0^\infty z^3 e^{-rz}\, dz = \frac{6}{r^4} \quad \text{and} \quad \sum_{r=1}^{r=\infty} \frac{1}{r^4} = \frac{\pi^4}{90}$$

But by Eq. (2-11) and the definition of σ we have

$$E = bT^4 \quad \text{and} \quad \sigma = \frac{bc}{4}$$

hence,

$$\sigma = \frac{2}{15} \frac{\pi^5 k^4}{c^2 h^3} \tag{2-40}$$

Thus h may be determined from a knowledge of σ, k, and c; or, if Eqs. (2-39) and (2-40) are both used, h and k may be determined from a knowledge of the black-body constants and the velocity of light.

2-10. Experimental Verification of Planck's Law.—The determination of the energy distribution in the spectrum of black-body radiation involves the use of a spectrometer with some energy-measuring device replacing the photographic plate. Such a device may be a bolometer, radiometer, radiomicrometer, or thermopile. The relative merits of these different instruments in their modern forms are discussed in books dealing with infra-red technique such as those by Rawlins and Taylor,[1] Lecomte,[2] or Schaefer and Matossi.[3] In general a sensitive linear-type thermopile is found to be the most satisfactory. Since the most interesting portion of the spectrum—that in which the energy density is a maximum—occurs in the infra-red for temperatures easily available, the spectrometer must be suited for the analysis of infra-red radiation. The difficulty and expense of manufacturing achromatic lenses which do not absorb a large portion of this radiation necessitate the use of concave mirrors in such a spectrometer. Mirrors are achromatic, and if the path of the radiation is always close to the axis, they are but slightly astigmatic; furthermore, metal or metal-on-glass mirrors have a very high reflecting power (90 to 98 per cent) in the infra-red beyond 2μ.

The refracting prism may not be of glass, for even 1 cm. thickness is practically opaque to wave lengths greater than 3μ. Carbon disulfide, quartz, fluorite, and rock salt (NaCl) are especially useful for prisms, each one having certain advantages for use at particular wave lengths, such as large dispersion or freedom from absorption. Quartz has a characteristic absorption band at 2.95μ and becomes opaque at 4μ. Fluorite is very transparent from 0.2 to 10μ, but it is difficult to obtain in large pieces. Rock salt is almost uniformly transparent from 0.2 to 12μ but becomes opaque at 20μ. Sylvite exhibits small dispersion from 5 to 10μ and has absorption bands at 3.18 and 7.08μ, but it is very useful between 10 and 20μ—if it can be obtained at all.

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[1] RAWLINS and TAYLOR, "Infra Red Analysis and Molecular Structure," Cambridge University Press (1929).

[2] LECOMTE, "Le Spectre Infra Rouge," Presses Universitaires de France (1928).

[3] SCHAEFER and MATOSSI, "Das Ultrarot Spektrum," Springer (1930).

One method of procedure is the isothermal; the temperature of the radiator is held constant and the energy density, or a quantity proportional to it, is measured as the wave length is changed; then the temperature is altered and the measurements repeated. Or the isochromatic method may be used, wherein the energy in one wave-length region at a time is measured as the temperature is varied. In either case, for high precision, mere inspection of the data is not sufficient to pick the wave length at which the energy is a maximum, so that $\lambda_{\max} T$ may be found. Instead, the expression of Planck, Eq. (2-35), or that of Wien, Eq. (2-27) is rewritten in such a form that the constant hc/k, which we shall call c_2, and which is equal to a constant times $\lambda_{\max} T$, may be computed by a method of successive approximations. In Planck's expression, as we saw from Eq. (2-39), $c_2 = 4.9651\lambda_{\max} T$; on differentiating Wien's equation to find the value of λ at which the energy is a maximum upon that law, we obtain $c_2 = 5\lambda_{\max} T$. It has been found that c_2 remains more nearly constant with Planck's form of the energy-distribution equation than with that of Wien.

For extremely long wave lengths, where even sylvite becomes opaque, the isochromatic procedure may be used by means of the method of *Reststrahlen*, or residual rays, which was discovered by Rubens and Nichols.[1] In using this principle, the radiation is reflected several times from plates of quartz, fluorite, or rock salt; those wave lengths which are absorbed in transmission are reradiated back by a supposed molecular resonance mechanism, so that the crystals show a high selective-reflection coefficient. In this way certain particular wave lengths may be sorted out and the energy contained in them measured as a function of the temperature.

The validity of Planck's radiation law, as opposed to that of Rayleigh and Jeans or that of Wien, has been demonstrated by a number of observers over a wide range of temperature and wave length; notably by Paschen,[2] Lummer and Pringsheim,[3] Warburg,[4] Coblentz[5] and

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[1] Rubens and Nichols, *Wied. Ann.*, **60**, 418 (1897).

[2] Paschen, *Berlin. Ber.* **21**, 403, 959 (1899); *Ann. Physik.*, **4**, 277 (1901).

[3] Lummer and Pringsheim, *Verh. Deut. Physik. Ges.*, **1**, 23, 215 (1899); **2**, 163 (1900).

[4] Warburg, *et al.*, *Verh. Deut. Physik. Ges.*, **18**, 1 (1916); and references there given.

[5] Coblentz, *Bur. Standards Bull.*. **10**, 1 (1914); **13**, 459 (1916); **15**, 529 (1920).

Rubens and Michel.[1] An accurate investigation of this kind is far from easy to carry through. The radiator and receiver are not perfectly black, the temperature measurements are difficult to make, absorption by water vapor and carbon dioxide in the air distorts the curves, the index of refraction and its variation with temperature for the material of the prism must be very accurately known, the absorption of the prism and the reflecting power of the mirrors must be carefully measured and allowed for, a correction must be applied because a range of wave lengths enters the final slit and this range is different in different parts of the spectrum, etc. But as a result of these experiments, it has been shown beyond all reasonable doubt that throughout the spectrum from 0.5μ to 50μ, and from liquid-air temperatures to 2200° abs., Planck's expression fits the observed spectral energy distribution more closely than any other expression which has been proposed. The most probable value of the constant c_2 is:

$$c_2 = 1.432 \pm 0.003 \text{ cm. deg.}$$

from which

$$\lambda_{\text{max}} T = \frac{c_2}{4.9651} = 0.2884 \pm 0.0006 \text{ cm. deg.}$$

2-11. Experiment on the Black-body Radiation Spectrum.—The instrument used in this type of experiment is an infra-red spectrometer, which is shown diagrammatically in Fig. 2-9. Such an instrument may be purchased from manufacturers of spectroscopic apparatus. It is also possible to build a satisfactory substitute from an old spectrometer of the ordinary type after removing the collimator and telescope. The Wadsworth mirror M_3 and the salt prism are mounted on the spectrometer table which must be fitted with an arrangement for rotating it very slowly and uniformly. The rotation must be accurately measurable to about 0.005°. Such an arrangement can be made very simply by fastening an arm 10 or 15 cm. long to the spectrometer table. The extremity of this arm is pressed by means of a spring firmly against the end of the screw of a micrometer caliper whose frame is attached rigidly to the fixed arm of the spectrometer. The bearing surface on the arm, which is in contact with the end of the caliper screw, should be a small ball bearing soldered into a depression in the face of the end of the arm opposite the screw. Such an arrangement is readily capable of rotating the table through 6° or 8°, which is more than is necessary, and the rotation of the table can be read to the required degree of accuracy.

The only requirement on the mirror M_1 is that it should have a large aperture in order that the intensity of the light from the black body focused on the slit S_1, may be as great as possible; a ratio of diameter to focal length of 1:10 is quite satisfactory. The slit S_1 is an ordinary-quality adjustable slit, and S_2 may be simply the slit supplied with the thermopile itself. To facilitate adjustment, the jaws of this slit may be covered with white paper so that the spectrum formed in this plane may be easily observed. The thermopile should be of the linear type and for the best results the most sensitive obtainable. Its terminals are connected through low-resistance leads to a galvanometer of high voltage sensitivity, such as G_1 (Fig. 2-5) which was used in the verification of Stefan's law. The deflections of this galvanometer during the course of the experiment are proportional to the emissive power of the black body and hence to the energy density in black-body radiation. The thermopile and the slit S_1 should be mounted rigidly with respect to the spectrometer and in approximately the positions shown in Fig. 2-9. All the mirrors should be front silvered. M_3, which is known as a Wadsworth mirror, is a plane mirror about 15 cm. long and with a width at least equal to the height of the prism. This mirror is mounted on the spectrometer table, resting upon its longer edge as shown, and its angle of inclination to the table should be adjustable. M_2 and M_4 are similar concave mirrors, 4 or 5 cm. in diameter and with focal lengths of about 30 cm., which are situated at distances equal to their focal lengths from S_1 and S_2, respectively, as shown in the diagram. These mirrors should be mounted rigidly with respect to the spectrometer but with sufficient adjustments for lining up and focusing.

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[1] Rubens and Michel, *Physik. Zeits.*, **22**, 569 (1921).

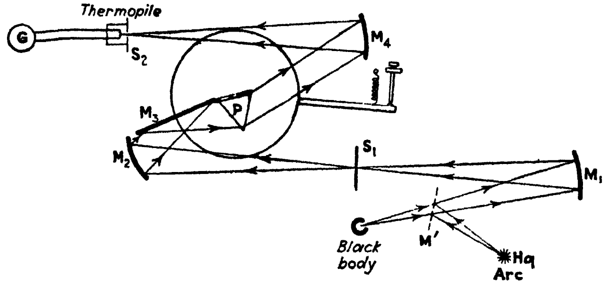


FIG. 2-9.—Diagrammatic representation of an infra-red spectrometer.

The rock salt prism, if such a one is used, must be obtained from a dealer in spectroscopic apparatus. As will be seen later it is necessary to know the prism angle in order to calculate the wave length striking the thermocouple slit in terms of the setting of the micrometer screw which adjusts the table. This angle may be measured on a spectrometer equipped with a Gauss eyepiece as is described in any text on experimental optics. The surfaces of these salt prisms deteriorate rapidly unless kept free from moisture; hence they should always be stored in a desiccator. The surfaces may be restored, if they deteriorate, by polishing on fine wet silk stretched over a piece of plate glass. The prism angle should be remeasured after polishing as it is frequently materially altered.

In the preliminary adjustments, the image of a mercury arc is thrown on S_1 by means of the mirror M', which is removed when the radiation from the black body is being analyzed. The parallel light leaving M_2 is reflected from M_3 and impinges on the face of the prism. After leaving the prism it is focused by M_4 on the white-paper surfaces of the jaws of S_2. The prism alone is then rotated and the mirror M_4 adjusted till the mercury green line ($\lambda = 0.5461\mu$) is focused upon the slit of the thermopile at minimum deviation. In this condition for a small rotation of the prism, in either sense, the green line appears to move in the same direction. As is shown in texts on optics, at minimum deviation half the deviation of the ray occurs on entering the prism and half on leaving it; the ray when passing through the prism is parallel to the base.

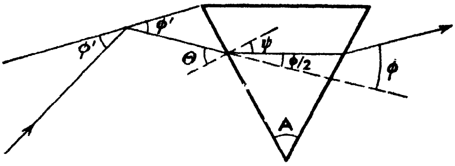


Fig. 2-10.—The path of a ray through the Wadsworth mirror and prism combination, at minimum deviation.

Because of the presence of the mirror M_3, the light reaching the slit of the thermopile has always passed through the prism at minimum deviation for any rotation of the prism and mirror system together. The path of a ray at minimum deviation is shown in Fig. 2-10. Let us say that ϕ' is the angle between the mirror surface and the light rays striking it, and let the angle between the reflected ray and the normal to the prism face be θ. If ψ is the angle between the inward normal and the ray in the prism at minimum deviation, we have the following relation between θ and ψ and the index of refraction, n, of the material composing the prism:

$$\sin\theta = n \sin\psi$$

As may be seen from Fig. 2-10, we may write

$$\sin\theta = \sin\left(\psi + \frac{\phi}{2}\right) = \sin\left(\frac{A + \phi}{2}\right)$$

where $\phi/2$ is the deviation of the ray on entering the prism, and $2\psi = A$, for the ray in the prism is perpendicular to the bisector of A. Replacing ψ by $A/2$ in the first expression also, we obtain for n:

$$n = \frac{\sin\left(\dfrac{A + \phi}{2}\right)}{\sin(A/2)} \tag{2-41}$$

The ray suffers a deviation $2\phi'$ clockwise on reflection from the mirror and a deviation ϕ counterclockwise on passing through the prism, so the ray at minimum deviation is changed in direction by an angle $2\phi' - \phi$ by the prism-mirror combination. For any arbitrary rotation of the prism-mirror system through an angle which we may call ω in a clockwise direction, the change in direction undergone by the ray leaving the mirror is $2(\omega + \phi')$, and the deflection produced by the prism, if the ray passes through it at minimum deviation, is $\phi + 2\omega$ in the opposite sense, hence the total deviation of the ray passing through the prism at minimum deviation is again $2\phi' - \phi$. Thus the total deviation of this particular ray is independent of the angular rotation of the prism-mirror system. The preliminary adjustment has assured that the ray bent through this angle strikes the slit in front of the thermopile; therefore, for any position of the prism-mirror system, the light striking the slit has passed through the prism at minimum deviation and Eq. (2-41) is applicable to determine the angle ϕ, if A and the index of refraction n for the particular wave length are known. Or conversely, if ϕ and A are known, n may be found, and from the dependence of n on the wave length, which is assumed to be known, the wave length can be calculated. The calculation is performed in the first order for the calibration of the instrument and in the second order for the reduction of table rotations into wave lengths.

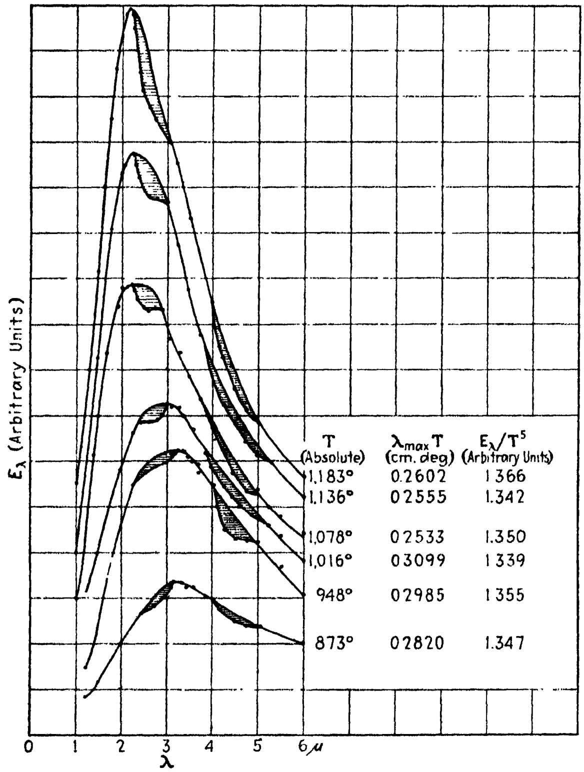
After the preliminary adjustments for minimum deviation have been accomplished, the mirror M' is removed temporarily and the black body is placed in position and heated to about 800° abs. The black body described in connection with Stefan's law may be used in this experiment also, and the measurements of its temperature are carried out as before. With the black body focused on S_1, the table is rotated by means of the screw till the region of the spectrum beyond the red is over the slit of the thermopile. The screw is then adjusted till the galvanometer deflection is a maximum, and the slits S_1 and S_2 are narrowed symmetrically about their centers, keeping their widths approximately equal till the galvanometer deflection is only 1 or 2 cm. The slits are then as narrow as can be worked with conveniently. The final calibration is the measurement of the number of degrees rotation of the table, which is half the number of degrees rotation of the minimum deviation beam by the prism, produced by one rotation of the screw. As the angle is small the relation between these quantities may be taken as linear, and a series of determinations of the table rotation, as measured by the angular scale on the spectrometer, are made for about 1-cm. motion of the screw. The averages of these quantities are taken and reduced to degrees rotation of the minimum deviation ray by the prism per smallest screw division; this quantity is written as B in the following calculations.

For obtaining the fiducial setting of the screw from which the subsequent settings will be measured, the mirror M' must be returned to position and the image of a mercury arc again cast on S_1. A series of settings of the mercury green line upon the slit of the thermopile is then made, and the average of the screw readings taken as a measure of the fiducial angle ϕ_0. These settings have to be made visually, for with an ordinary mercury arc there is not sufficient energy in the green line to affect the thermopile. The mirror M' is then removed permanently and the spectrometer is shielded with a light wood or cardboard box. This box must contain an opening opposite the slit for the entrance of light from the mirror M_1 and a hole for the emergence of the arm carrying the micrometer screw with which the adjustments of the table are made. After the temperature inside the box has reached equilibrium, and the galvanometer fluctuations have ceased, the main series of energy measurements in the black-body spectra are made. With the black body at about 850° abs., the table is rotated and micrometer-screw and galvanometer readings taken at suitable intervals, which of course should be closely spaced in the neighborhood of the maximum deflection, till the entire range of the spectrum containing appreciable energy has passed over the slit of the thermopile. The temperature of the black body is then elevated 50° or 100° and a second run taken. This procedure may be continued up to temperatures of 1200° or 1400° abs. Above this region the coating of the black body deteriorates fairly rapidly.

The screw readings are most conveniently reduced to wave lengths by the tabular method outlined below. The first entry in the table is the wave length of the fiducial mercury green line in the wave-length column. From the table at the end of the chapter log n is obtained for this wave length. The calculations are then worked backwards, using Eq. (2-41) as $\log n = \log \sin \dfrac{A + \phi}{2} - \log \sin A/2$, in the tabular form up to the column $A + \phi$ for which the entry is $A + \phi_0$. The entries under the headings Δ screw and $\Delta\phi$ are zero, and the entry in the first column is the fiducial screw setting. The settings for which the wave lengths are to be calculated are then entered in the screw column, and the Δ screws (the differences between these settings and the fiducial setting) are calculated and entered in the second column. These values are then multiplied by the screw-deviation factor B and entered in the third column. The entries in the column $A + \phi = A + \phi_0 \pm \Delta\phi$ are obtained by adding or subtracting the values of $\Delta\phi$ from the fiducial $A + \phi_0$, depending on whether increasing screw readings correspond to decreasing or increasing values of the deviation. The entries in the subsequent columns are made in the order indicated. The values of the wave lengths corresponding to the entries in the column log n are obtained by interpolating in the table at the end of the chapter, or from the curve obtained by plotting the table.

Screw	Δ screw	$\Delta\phi = B \cdot \Delta$ screw	$A + \phi$	$\frac{A + \phi}{2}$	$\log \sin \frac{A + \phi}{2}$	$\log n$	wave length

From this correlation between the screw settings and the wave length, the galvanometer deflections, which are proportional to the monochromatic emissive powers of the black body, may be plotted as functions of the wave length, and curves similar to those in Fig. 2-11 are obtained. The portions of the curves above the hatched areas, which represent the selective atmospheric absorption which has been referred to, are sketched in to make the curve smooth through those regions. The values of $\lambda_{\max} T$ may be obtained with all warrantable accuracy by inspection, for the many corrections which were mentioned in connection with precision work have been neglected. From the average value of $\lambda_{\max} T$ and the values of σ and c which have been obtained, the constant h may be calculated by means of Eqs. (2-39) and (2-40) after the elimination of k. However, as σ is a difficult quantity to measure, a more accurate value of h may be found from Eq. (2-39) alone, using the value of k



T (Absolute)	$\lambda_{max}T$ (cm. deg)	E_λ/T^5 (Arbitrary Units)
1,183°	0.2602	1.366
1,136°	0.2555	1.342
1,078°	0.2533	1.350
1,016°	0.3099	1.339
948°	0.2985	1.355
873°	0.2820	1.347

FIG. 2-11.—Typical black-body energy-distribution curves for various temperatures, obtained by the simple method described in the text. The shaded areas represent atmospheric absorption. The ordinates are galvanometer deflections, which are proportional to the energy density and to the emissive power. The figures at the right indicate the order of accuracy to which Wien's laws are verified by this experiment.

determined from the experiment in Chap. IV. A series of curves may also be plotted using E_λ'/T^5, where E_λ' is the galvanometer deflection, as ordinates and the values of λT as abscissas. These curves should then be superposed on one another in accordance with Wien's displacement laws. The actual agreement which may be expected is shown in

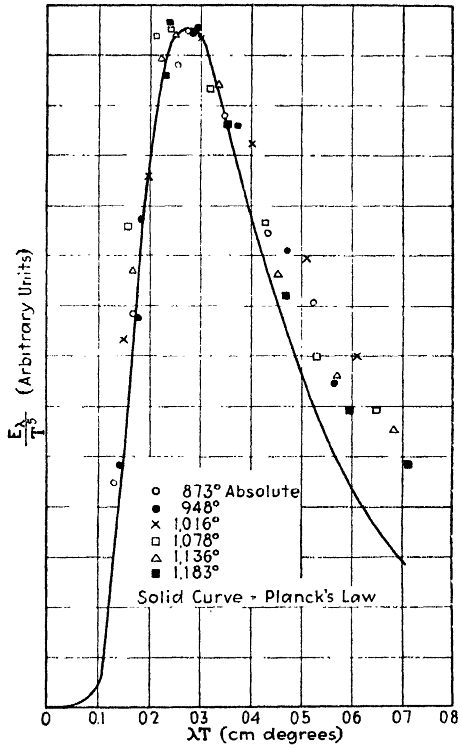


FIG. 2-12.—The data of Fig. 2-11, corrected for atmospheric absorption, are here plotted to show that E_λ/T^5 is a single function of λT, to the order of accuracy of the procedure. The solid line is drawn from Planck's equation, $E_\lambda = c_1\lambda^{-5}/(e^{c_2/\lambda T} - 1)$, where $c_2 = 4.9651\lambda_{\max}T$, and $\lambda_{\max}T$ is taken as the average of the values given in Fig. 2-11. The constant c_1 has been adjusted so that the curve fits the average of the experimental points at the peak, since E_λ is in arbitrary units. The departure of the experimental points from the Planck curve at the larger values of λT is due largely to neglect of the corrections to be applied because of the finite width of the thermopile slit.

Fig. (2-12). These experimental points may be compared with the Planck expression by plotting this expression as

$$y = \frac{c_1}{x^5\left(e^{\frac{c_2}{x}} - 1\right)}$$

Here $y = E_\lambda'/T^5$, $x = \lambda T$, $c_2 = 4.9561\ (\lambda_{\max} T)_{\text{ave}}$, and c_1 is a constant which must be chosen so that the theoretical curve is in agreement with the experimental points at some arbitrary place, say at the maximum of the curve. That is, c_1 is chosen so that the theoretical curve passes through $(E'_{\lambda_{\max}}/T^5)_{\text{ave}}$ and $(\lambda_{\max}T)_{\text{ave}}$. The solid line in Fig. 2-12 represents this curve, and the observed departure of the experimental points from it is adequately accounted for by the slit width and other corrections which have been neglected in this treatment.

2-12. Theories of Radiation Phenomena.—The two radiation phenomena discussed in Chap. I—the velocity with which radiation travels and the pressure which it exerts—can both be explained quite satisfactorily on the basis of either a wave or particle theory. In the first of these, however, the evidence distinctly supports the electromagnetic theory, for it actually predicts the numerical value of the velocity of propagation, whereas this quantity appears as an unexplained constant on the simple particle theory. There are many other phenomena exhibited by radiation and most strikingly demonstrated by visible light, such as interference, diffraction, and polarization, which are very difficult to explain on the conception of a beam of light as a stream of particles, for which we have adopted the name photons or quanta. These phenomena, which lie outside the range of this book, are described from the wave point of view in texts on optics, and the electromagnetic theory accounts for all of them in a very satisfactory and complete manner.

On the basis of the arguments which were introduced at the beginning of this chapter, the two fundamental laws of thermodynamics account for the general behavior of black-body radiation up to a certain point. However, the classical radiation theory, associated with electromagnetic waves, fails at this stage. To account fully for the energy distribution in the spectrum of black-body radiation, it is necessary to introduce some assumptions which are at variance with the application of classical mechanics to the electromagnetic theory. These all involve a break with the classical picture of radiation. They are associated fundamentally with a photon conception of light, and we are confronted with the fact that when dealing statistically with these photons we may not use the classical statistics. This is shown by Bose's derivation of Planck's equation. Later chapters will provide further justification for both the wave and particle aspects of radiation. A satisfactory theory must result in a fusion of these two aspects.

The applicability of the two concepts may roughly be classified as follows: For those phenomena dealing with the propagation of radiation, the wave concept is most conveniently used; and for those phenomena connected with the emission and absorption of radiation, the particle or photon concept is almost indispensable. These two opposed concepts may be reconciled, mathematically at least, by interpreting the electromagnetic waves as a phantom or virtual wave structure which effectively guides the photons or directs their trajectories. This phantom radiation field is calculated as usual on the basis of the classical electromagnetic equations. The light intensity for a particular wave length at a point in space which these equations predict is then to be interpreted as either a density function for photons or a probability expression representing the chance of finding a photon of the proper frequency at that particular place. If the calculated intensity is large, many photons pass that place per second; if it is small, there is very little likelihood of ever observing a photon there. The phenomenon of polarization, which is so readily explicable on any transverse-wave theory, may be dealt with upon a particle theory by the association of an angular momentum with each photon. This angular momentum vector is equal to $h/2\pi$ and is directed either parallel or antiparallel to the trajectory, thus giving rise to the phenomena which on the wave concept are spoken of as right- or left-circular polarization. This finds a fairly close analogy with the similar angular momentum, or spin vector, which it will be found necessary to associate with an electron. An interesting résumé of this aspect of radiation phenomena has been given by Brillouin.[1] This modern conception of the significance of electromagnetic waves—that they merely determine the path of a corpuscular photon—is of great importance, for it supplies a clue to the interpretation to be placed on the de Broglie waves associated with electrons and protons, which will be discussed in Chap. V. Such non-electromagnetic waves are analogously considered as the guides for the material particle's trajectory.

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[1] BRILLOUIN, "Les Statistiques Quantiques," Chap. III, Presses Universitaires de France (1930).

Variation with Wave Length of the Logarithm of the Index of Refraction of Rock Salt (NaCl) in Air at 20°C.[1]

Wave length, μ	$\log_{10} n$	Wave length, μ	$\log_{10} n$
0.5461 (Hg green)	0.18965	2.6505	0.18330
.5893 (Na yellow)	872	.9466	317
.6400	792	3.2736	290
.6874	732	.5359	273
.7604	662	.6288	266
.7858	641	.8192	252
.8835	581	4.1230	229
.9033	571	.7120	178
.9724	541	5.0092	151
1.0084	527	.3009	124
.0540	513	.8932	068
.0810	504	6.4825	.17997
.1058	497	.80	955
.1420	487	7.0718	924
.1768	478	.22	903
.2016	473	.59	856
.2604	461	.6611	846
.3126	451	.9558	801
.4874	425	8.04	794
.5552	417	.8398	665
.6368	407	9.00	638
.6848	402	.50	603
.7670	394	10.0184	453
2.0735	370	11.7864	076
.1824	361	12.50	.16899
.2464	357	12.9650	779
.3560	349	13.50	631

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[1] Data by Langley, Paschen, and Rubens, as given in Glazebrook, "Dictionary of Applied Physics," vol. IV, p. 141 (1923).

CHAPTER III

THE ATOMICITY OF MATTER AND ELECTRICITY

3-1. Early Developments of Atomic Theory.—The concept of the atomicity of matter is much older than the experimental evidence warranting it. One school of Greek philosophy considered that all physical entities were composed of very small discrete particles, but as these speculations rested on no experimental foundation they hardly can be considered as constituting a physical theory. At the beginning of the eighteenth century, Daniel Bernoulli suggested that the various mechanical properties of fluids could be explained on the assumption that they were made up of very large numbers of infinitesimal particles moving at random with great velocities. The simple properties of gases were dealt with quite adequately in his "Hydrodynamica" (1738), which may be considered the first introduction of the kinetic theory of matter. This hypothesis cannot be said to have acquired any general acceptance, however, nor can the atomic theory be considered to have reached a stage where it had been quantitatively tested until after the work of Proust, Gay-Lussac, Dalton, and Avogadro.

About the year 1806 the chemical law known as *the law of definite proportions* was experimentally established, largely through the work of Proust. This law states that "the proportions in which two elements combine cannot vary continuously." It was found that 18 grams of water were always composed of 16 grams of oxygen and 2 grams of hydrogen. Compounds of carbon and hydrogen were known, and it was shown that 16 grams of methane contained 12 grams of carbon and 4 grams of hydrogen, and also that 28 grams of ethylene were made up of 24 grams of carbon and 4 grams of hydrogen. These quantitative analyses were not very accurate, but they were sufficient to show that while carbon and hydrogen could combine in the proportions of 6 to 1 and of 3 to 1 by weight, they could not form chemical compounds of composition varying continuously between these values.

The knowledge of these combining weights gained from the study of such compounds as methane, ethylene, water, carbon dioxide, and ammonia led Dalton to formulate *the law of multiple proportions.* This may be stated as follows: "If any two compounds containing the elements A and B are considered and if a comparison is made between the masses of B found in combination with, say, a unit mass of A, they will be found to be in a simple ratio to one another." Taking our examples of methane and ethylene, the masses of carbon in combination with the same mass of hydrogen are found to be in the ratio of 2 to 1. Further, it was discovered that hydrogen and oxygen combine in the ratio of 4 to 32 to form water, and that carbon and oxygen combine in the ratio of 12 to 32 to form carbon dioxide. The ratio of the combining weights of hydrogen and carbon with oxygen is thus 1:3, the same ratio as the combining weights of hydrogen and carbon in methane.

Dalton[1] made what appeared to be the simplest assumption upon this evidence: that the molecules of compounds were made up of small integral numbers of the atoms of the elements forming the compounds. He gave the following definitions and rules:

1 atom of A + 1 atom of B = 1 molecule of C	binary
1 atom of A + 2 atoms of B = 1 molecule of D	ternary
2 atoms of A + 1 atom of B = 1 molecule of E	ternary
Etc.	

> When only one combination of two bodies can be obtained, it must be presumed to be a binary one, unless some cause appear to the contrary.
>
> When two combinations are observed, they must be presumed to be a binary and a ternary.
>
> When three combinations are obtained, we may expect one to be a binary and the other two ternaries. Etc.

Of course, exceptions can be found to these rules, but they may be taken as a starting point. Dalton used them to calculate the weights of various atoms in terms of the weight of the hydrogen atom.

In about 1810, Gay-Lussac showed that the dependence of the density upon the pressure and the temperature was the same for all ordinary gases, to the order of accuracy of his measurements. Consequently, the number of molecules per unit volume for all these gases, which may be termed *perfect gases,* varies in the same way with the pressure and with the temperature. Hence if at some particular temperature and pressure the number of molecules per unit volume for two gases is the same, it must be the same for all temperatures and pressures. He also found a simple relation between the combining volumes of gases by noting that under similar conditions of temperature and pressure the volumes of the gases which appear or disappear in a reaction are in simple ratios to one another.

From these data, all that would be needed to establish the rules of Dalton for gases would be to have equal numbers of molecules of different gases occupy the same volumes under similar conditions of temperature and pressure. For if two volumes of hydrogen combine with one volume of oxygen to form the compound water vapor, and if equal volumes of each gas contain equal numbers of molecules, each molecule of oxygen has combined with two molecules of hydrogen. As a matter of fact, two volumes of water vapor are formed, so if the simplest molecule for water is assumed, namely a ternary molecule in Dalton's nomenclature, we must suppose that each hydrogen and each oxygen molecule is made of two atoms. We should write the equation

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[1] Dalton, "New Systems of Chemical Philosophy," Bickerstaff, Manchester (1808).

$$2\,H_2 + O_2 = 2\,H_2O$$

where the coefficients correspond to the combining volumes.

The hypothesis that equal volumes of gases under the same conditions of temperature and pressure contain equal numbers of molecules was made by Avogadro a year or so later. The hypothesis was not accepted immediately, nor was the demonstration that Dalton's theory was in accord with experiment accepted as proof that atoms existed. However, it constituted the first step in the establishment of the atomic theory of matter. The fundamental truth of the theory has been as well verified subsequently as it is possible for any theory to be verified by inductive methods. Almost all the experimental facts mentioned throughout this book may be considered as direct or indirect proofs of the theory.

On the basis of the work of these early investigators, we may write in various ways the equation describing the behavior of a perfect gas. If we choose a unit mass of gas and write the volume that it occupies as v, its pressure as p, and the absolute temperature (centigrade temperature plus 273.2°) as T, we have

$$pv = aT \tag{3-1}$$

where a is a constant. If, on the other hand, we choose a mass of gas equal to its molecular weight (*i.e.*, a gram-molecule), this mass will contain the same number of molecules and occupy the same volume for all gases. Multiplying the above equation by M, the molecular weight, and writing V for Mv and R for Ma, we have

$$pV = RT \tag{3-2}$$

where R is a universal constant known as the *gas constant.* If p is measured in dynes per square centimeter and V in cubic centimeters, R is found by experiment to have the value 8.314×10^7 ergs per degree. If we let N be the number of molecules in 1 gram-molecule and m the mass of a molecule, $M = Nm$, and putting this in Eq. (3-1), after multiplication by M, we find

$$pNmv = RT$$

But mv is the volume occupied by one molecule and its reciprocal is the number of molecules per unit volume, which we may write as n. So writing k for R/N we obtain another form of the gas law.

$$p = nkT \tag{3-3}$$

These are all expressions of the same fundamental facts, but different forms will be found convenient to use in different instances.

The early atomic theory had nothing to say in regard to the sizes or masses of the atoms or molecules. Obviously they must be small enough to give the continuous character observed in matter on a large scale; the atomic "grain" must not be of an order of magnitude to be observed in ordinary physical measurements, or it would have been discovered at a very early date. Estimates of the upper limits of atomic dimensions can be made by measuring the thickness of the thinnest available films of various substances. A known weight of gold may be beaten out into a film thin enough to appear green by transmitted light; knowing the mass and density, a measurement of the area of the film permits the thickness to be calculated. Films of gold may be prepared one ten-thousandth of a millimeter (10^{-5} cm.) in thickness, and as these films appear quite homogeneous they are undoubtedly several atoms thick. Thus a gold atom must occupy a volume much less than 10^{-15} cm.^{3}. Still smaller upper limits to atomic dimensions can be obtained from measurements of soap and oil films. When a soap film is produced, it is often noticed that in addition to the ordinary iridescent colors black areas with well-defined edges appear. They are not actually holes, but the bubble or film generally breaks soon after their appearance. If the soap solution is made of pure ammonium oleate and glycerine, as described by Lawrence,[1] films containing these black regions may be kept for long periods of time, and the thickness of the areas may be measured with an interferometer or by measuring their reflecting power for light. The thinnest of these black areas have a thickness of approximately 5×10^{-7} cm. They are apparently quite homogeneous and probably at least two molecules thick. These molecules are complicated organic compounds of a chain type containing many atoms. At a very conservative estimate we can say that the molecular volumes are less than 2×10^{-20} cm.^{3}, and the volumes of the individual atoms are much less than that.

It is easier to produce these thin films on a supporting surface such as water. Very thin oil films, free from thick spots and with well-defined edges, may be produced by allowing a drop of a dilute solution of a highly refined oil in benzene to fall upon a water surface. The benzene evaporates rapidly leaving the oil film on the water. If the experiment is performed in a shallow dish, powdered talc may be sprinkled over the surface and distributed horizontally by gentle blowing. Where the particles of talc come in contact with the oil film, their motion is stopped and the outline of the film is given very sharply. The area of the surface may be measured accurately, and, if the mass and density of the oil are known, the thickness of the film can be computed. In this way films may be prepared with a thickness of but little over 10^{-7} cm. If these are monomolecular films, the dimension of the oil molecule normal to the surface is of the order of 10^{-7} cm. From the density of the oil the mass of a sphere of this size can be calculated, and if the composition of the oil is known, the approximate mass of a hydrogen atom can be computed. If such an oil as glycerine trioleate ($C_{57}H_{104}O_6$) is used, the mass of a sphere equal in diameter to the thickness of the film is found to be of the order of 10^{-21} grams. The ratio of the mass of a hydrogen atom to the mass of this molecule is 1:884, so the mass of a hydrogen atom is of the order of magnitude of 10^{-24} grams. This is of the correct magnitude as will be seen when accurate methods of measuring these masses are discussed in detail.

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[1] LAWRENCE, "Soap Films," Bell (1929).

3-2. Brownian Motion.—The most direct evidence for the existence of individual particles of these dimensions comes from two general types of phenomena. The first of these is connected with radioactive disintegration, which will be discussed in a later chapter. The other phenomenon that brings out most clearly the existence of individual atoms is that known as *Brownian motion*.

In 1827, shortly after the manufacture of the first achromatic objectives, Robert Brown[1] observed, under high magnification, an agitation of minute pollen grains suspended in water. He noted this random motion of agitation for small particles of a large variety of organic and inorganic substances. He did not claim the original discovery of this phenomenon as it had been observed with less certainty before by men with poorer microscopes, but the experiments he performed showed very convincingly that this motion (which previously had been considered to be due to animalculae) was not caused by organisms moving of their own effort.

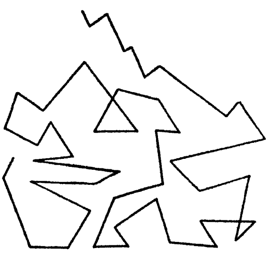

FIG. 3-1.—Two-dimensional trace of the net Brownian motion of a particle whose position is observed at the end of equal time intervals.

It was concluded by Wiener as early as 1863 that this agitation did not arise from any properties of the particles themselves or from any external cause, but that it was a property of the fluid state. A fluid which seems perfectly homogeneous and static only appears to be so because of the coarseness of our senses. We may assume from the permanent agitation of small particles suspended in a fluid that the fluid itself is in a condition of continuous random activity. The convincing experimental work on this phenomenon was performed many years after Brown's observations by a number of investigators, the chief among whom were Wiener,[1] Gouy,[2] Carbonelle,[3] and Bodeszewski.[4] Their results were only qualitative but they established the following facts:

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[1] BROWN, *Phil. Mag.*, 2d series, **4**, 161 (1828).

1. The motion of agitation does not depend on time, which shows that it is not due to some transient chemical or physical effect before the establishment of an equilibrium condition.
2. It is not dependent on the chemical nature of the fluid containing the particles.
3. The motion is not due to the jarring of the vessel holding the fluid.
4. The motion is apparently quite random. There is no tendency to steady drift as might be the case if it was due to thermal convection.
5. The magnitude of the motion is large if the particle observed is small.
6. The agitation increases with the temperature.
7. The magnitude of the motion is large if the viscosity of the medium is small.

We may form a picture of the mechanism of Brownian motion on the basis of the above facts. A colloidal particle very many times larger than the largest molecule is suspended in the fluid and is constantly subject to the bombardment of swarms of molecules. According to the laws of chance, the number striking the left side at any instant will not be equal to the number striking on the right, so there will be unequal forces on the two sides and the particle will move. At any instant the resultant force has an equal probability of being in any direction. As long as the molecular agitation persists, suspended particles will exhibit a random motion. If the particle is small, the chance of its experiencing an acceleration due to unequal bombardment will be large. If the molecules move more rapidly with increasing temperature, the unbalanced forces will be larger and the Brownian motion will increase. For a very viscous medium, the resistance to the motion of the particles is large and therefore the magnitude of the motion is small.

The correctness of the entire conception was thoroughly established by Perrin,[5] who made the first quantitative measurements of Brownian motion. The most important subsequent experimental work has been done by de Broglie[6] and by Millikan[7] and his collaborators working on the Brownian motion in gases. Quantitative work on the Brownian motion exhibited by large bodies has also been done, both experimentally and theoretically, by Zeeman and Houdyk,[1] Gerlach,[2] and by Uhlenbeck and Goudsmit.[3] Perrin's results may be considered conveniently in two categories. The first of these has to do with the number of suspended particles per unit volume found at various heights in a suspension. The second deals with the actual displacements of the suspended particles in a given time.

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[1] Wiener, *Ann. Physik. u. Chemie*, **118**, 79 (1863).

[2] Gouy, *J. Physique*, **7**, 561 (1888); *Comptes Rendus*, **109**, 102 (1889).

[3] Carbonelle, (Thirion), *Revue des Questions Scientific* Louvian, **7**, 5 (1880).

[4] Bodeszewski, *Dingler's Polyt. J.*, **239**, 325 (1881).

[5] Perrin, "Atoms" (transl. by Hammick), Constable (1923).

[6] De Broglie, *Comptes Rendus*, **146**, 624, 1010 (1908); **148**, 1316 (1909).

[7] Millikan, "The Electron," University Chicago Press (1927).
Fletcher, *Phys. Rev.*, **33**, 81 (1911).

3-3. The Law of Atmospheres.—It was shown by early work on osmotic pressure and on the chemistry of solutions that, if the molecules of a dissolved substance do not dissociate into positive and negative ions, they behave almost exactly as if the molecules of each substance occupied the whole volume of the container independently. That is, if a certain number of sugar molecules are dissolved in water, they exert a pressure on the walls equal to the pressure which they would exert at the same temperature if they occupied the volume of the solution in the form of sugar in a gaseous state. This is true to about the same approximation that the equation of a perfect gas is true for the common gases. The pressure exerted by the sugar molecules is independent of the pressure due to the other types of molecules present, as is also known to be the case in mixtures of gases. Further, as with gases, the pressure due to molecules under the same conditions of temperature and density is independent of the mass of the molecules. We might expect the perfect-gas laws to be capable of extension even up to the size of the particles that are observed in colloidal suspensions.

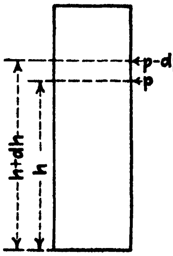

FIG. 3-2.—The change of pressure with height in a fluid.

Assuming that we may extrapolate the perfect-gas law to particles of this size, and that they behave as if they occupy the entire volume of the suspension independently of the suspending solution, we may proceed to calculate the number of particles per unit volume in the following manner: Consider a vertical column of unit cross section of the suspension, as in Fig. 3-2. At the height h, let the particle pressure be p. At a height $h + dh$, let the pressure be $p - dp$. The difference in pressure, $-dp$, is caused by the downward force exerted by the earth on the number of particles (n per unit volume) in dh, the force being $n\,dh\,m'g$, where m' is the effective mass of a particle and g is the gravitational acceleration. Therefore

$$-dp = nm'gdh$$

or substituting for p from Eq. (3-3),

$$-kTdn = nm'gdh$$

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[1] ZEEMAN and HOUDYK, *Proc. Acad. Amsterdam*, **28**, 52 (1925).

[2] GERLACH and LEHRER, *Naturwiss.*, **15**, 15 (1927).

[3] UHLENBECK and GOUDSMIT, *Phys. Rev.*, **34**, 145 (1929).

or

$$\frac{dn}{n} = -\frac{m'g}{kT}dh$$

Integrating between two heights where the particle concentration is n_1 and n_2, and setting $k = R/N$, we obtain

$$\log\frac{n_2}{n_1} = -\frac{m'gN}{RT}(h_2 - h_1)$$

or

$$\frac{n_2}{n_1} = e^{-\frac{m'gN}{RT}(h_2-h_1)}$$

This is the *law of atmospheres* which was first given by Laplace. The effective mass m' of a particle in a suspension is the difference between the mass of the particle and the mass of an equal volume of the liquid, or $m' = m\left(\frac{\rho - \sigma}{\rho}\right)$ where m is the mass of the particle, ρ is its density, and σ is the density of the liquid. We thus have for the expression giving the ratio of the numbers of particles of equal mass at the heights h_1 and h_2:

$$\frac{n_2}{n_1} = e^{-\frac{mgN}{RT}\left(\frac{\rho-\sigma}{\rho}\right)(h_2-h_1)} \tag{3-4}$$

Avogadro's number N (the number of molecules per gram-molecule) can be calculated from this expression, since all the other quantities are directly measurable.

Perrin tested this expression with colloidal suspensions of gum mastic and gamboge. These suspensions may be prepared by pouring an alcoholic solution of the gum into water. Clear spherical globules of the gum are formed by this method, but the sizes of the globules vary over a wide range. In order to obtain a suspension containing particles all of approximately the same dimensions, a lengthy process of fractional centrifuging must be resorted to. Such a uniform suspension is then placed in a small glass cell on a microscope stage. The depth of focus of a high-power microscope is very small, let us say, dh, and, if the area of the field is A, the region under observation is a disk-shaped volume Adh. The number of particles in the field of view at any one time is counted or photographed, so that the number per unit volume at a particular height in the suspension may be computed. The difference in height between regions where determinations are made is read directly from the scale on the microscope adjustment. In this way n_1, n_2 and $(h_2 - h_1)$ may be determined.

The measurements of the acceleration of gravity, the temperature, and the density of the suspending fluid are easily performed, but the determination of the mass and density of the particles presents difficulties. The density ρ was found by Perrin by three methods: (1) direct measurement of the density of the dry gum in bulk, (2) pycnometer determination of the density of the suspension, and (3) variation of the solution density by the dissolving of a salt and the determination of the solution density at which centrifuging effects no separation of the particles from the solution. These three methods of obtaining the density of the particles gave values which agreed with each other to better than one part in a thousand.

Knowing the density, a measurement of the volume occupied by a particle suffices to determine the mass. The particles used by Perrin were so small that they could not be measured directly with a micrometer microscope, so he resorted to three indirect methods: (1) If very dilute suspensions are allowed to evaporate from a microscope slide, the individual particles are pulled together and lined up by surface forces in groups one particle thick. If the area of such a patch is measured and the number of particles in it is counted, the volume of a single particle can be calculated on the assumption that the particles are spherical. (2) In a slightly acid solution (0.01 normal), the particles tend to stick to any surfaces which they strike. They may thus be collected on some small object the weight of which is accurately known; an estimate of the number of adhering particles is made, and from the weight of the object, after all the solution has evaporated, the mass of a single particle may be computed. (3) It was shown by Stokes that a sphere, small in comparison with the dimensions of the containing vessel but large in comparison with molecular dimensions, moving uniformly through a viscous fluid, experiences a retarding force Fv, where F is given by

$$F = 6\pi\eta a \tag{3-5}$$

Here a is the radius of the sphere, v its velocity, and η is the coefficient of viscosity of the fluid. Thus if η is known, and if the steady rate of fall v_g under the force of gravity is measured, we may calculate the radius of the sphere from the equality of the accelerating and retarding forces:

$$6\pi\eta a v_g = \tfrac{4}{3}\pi a^3(\rho - \sigma)g \tag{3-6}$$

Then the mass of the sphere is given by

$$m = \frac{4}{3}\pi\left(\frac{9}{2}\eta\right)^{\frac{3}{2}}\left(\frac{1}{(\rho-\sigma)g}\right)^{\frac{3}{2}}(v_g)^{\frac{3}{2}}\rho \tag{3-7}$$

These three methods of determining the mass of the particles gave values self-consistent to within about 1 per cent.

The foregoing discussion has shown how all the quantities occurring in Eq. (3-4) may be measured. Perrin worked with a large number of suspensions and, in the course of his observations, variations in all the factors were investigated. All of the suspensions were found to obey the exponential expression, Eq. (3-4), and the values for the constant N

lay between 6.5×10^{23} and 7.2×10^{23}. The consistency of these results is remarkably good when the difficulties in the measurement of the various factors are taken into consideration. The experiments not only substantiate very strongly the original assumptions, but they also provide a fairly accurate value for the number of molecules contained in a mass of a substance equal to its molecular weight, *i.e.*, 1 gram-molecule.

3-4. Displacement of Particles in Brownian Motion.—A further demonstration of the correctness of the concept of Brownian motion is afforded by measurements of the actual displacements of a suspended particle. The displacement in unit time may be estimated accurately by means of a coordinate screen in the field of view of a microscope, or the motion in a particular direction may be measured with a micrometer eyepiece or other suitable device. The theory correlating these displacements with other measurable quantities was first given by Einstein[1] and by von Smoluchowski,[2] but we shall consider a simpler derivation due to Langevin.[3]

On the basis of the kinetic theory, we may write the perfect-gas equation in a different form, if we assume that the pressure exerted by a gas is due to the bombardment of the walls of the vessel by the gas molecules which we suppose are moving at random. Let us imagine the gas to be in a cubical box, each edge of length L and oriented along the coordinate axes. If a molecule of mass m, moving with a velocity component u along the x-axis, collides perfectly elastically with the wall, this component is simply reversed in direction and the change in the momentum component is

$$mu - (-mu) = 2mu$$

In unit time the molecule travels a distance u and makes u/L collisions with the two opposite walls. Hence the change of the momentum component per unit time is $2mu^2/L$. The average rate of change in the x component of the momentum for all the molecules is $nL^3\ 2m\overline{u^2}/L$, where n is the number per unit volume, $\overline{u^2}$ is the average squared velocity component, and L^3 is the volume. Since force is equal to the rate of change of momentum, this expression gives the outward force on the two surfaces normal to the x-axis. The pressure on one surface is one half of this force divided by the area of the surface L^2, so that

$$p = nm\overline{u^2} = 2n\left(\frac{m\overline{u^2}}{2}\right)$$

The total velocity c of any molecule is the sum of its components u, v, w along the x-, y-, z-axes. By the Pythagorean theorem, $c^2 = u^2 + v^2 + w^2$;

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[1] EINSTEIN, *Ann. Physik*, **17**, 549 (1905); **19**, 371 (1906).

[2] VON SMOLUCHOWSKI, *Bull. Internat. Acad. Sci. Cracovie*, **7**, 577 (1906).

[3] LANGEVIN, *Comptes Rendus*, **146**, 530 (1908).

therefore, on taking average values, $\overline{c^2} = \overline{u^2} + \overline{v^2} + \overline{w^2}$. On our assumption of perfect randomness of motion, the average component velocities along the three axes are all equal, so that $\overline{c^2} = 3\overline{u^2}$. Therefore

$$p = \frac{2}{3}n\left(\frac{m\overline{c^2}}{2}\right) = \frac{2}{3}E \tag{3-8}$$

where E is the kinetic-energy content per unit volume of the gas. Comparing this with Eq. (3-3), $p = nkT$, we see that

$$\frac{m\overline{c^2}}{2} = \frac{3}{2}kT \tag{3-9}$$

Therefore

$$\frac{m\overline{u^2}}{2} = \frac{m\overline{v^2}}{2} = \frac{m\overline{w^2}}{2} = \frac{1}{2}kT \tag{3-10}$$

One-third of the kinetic energy is associated with the motion along any one of the three coordinate axes.

Let us now consider the equation of motion of a Brownian particle. Let us say that the unbalanced force along the x direction due to the unequal molecular bombardment is X, and let us suppose that the motion of the particle through the fluid is opposed by a viscous force which is proportional to the velocity. If the coefficient of this viscous drag is F, we may write Newton's second law of motion (that the mass times the acceleration is equal to the total force) as

$$m\frac{d^2x}{dt^2} = -F\frac{dx}{dt} + X \tag{3-11}$$

In the measurements of the position of the particle, we shall be interested mainly in the absolute value of the displacements, *i.e.*, the magnitude of the displacement regardless of sign, so it is desirable to alter this equation into one involving only squares of the coordinate x and its time derivative. If we multiply Eq. (3-11) by x and remember that

$$x\frac{d^2x}{dt^2} = \frac{1}{2}\frac{d^2}{dt^2}(x^2) - \left(\frac{dx}{dt}\right)^2$$

we obtain

$$\frac{1}{2}m\frac{d^2}{dt^2}(x^2) - m\left(\frac{dx}{dt}\right)^2 = -\frac{F}{2}\frac{d}{dt}(x^2) + Xx \tag{3-12}$$

Considering the average of each of these terms over a long time, we see that the second term on the left is $m\overline{(dx/dt)^2}$, which is equal to kT by Eq. (3-10), and the average of the second term on the right is zero, since X and x vary independently and so their product is as often positive as negative. Therefore, writing z for $\frac{d}{dt}\overline{x^2}$, we have

$$\frac{m}{2}\frac{dz}{dt} - kT = -\frac{F}{2}z \tag{3-13}$$

Separating the variables,

$$\frac{dz}{z - \frac{2kT}{F}} = -\frac{F}{m}dt$$

and integrating from zero to z and from zero to t, we obtain

$$\left[\log\left(z - \frac{2kT}{F}\right)\right]_0^z = -\frac{F}{m}\Big[t\Big]_0^t$$

$$\log\left(z - \frac{2kT}{F}\right) - \log\left(-\frac{2kT}{F}\right) = -\frac{F}{m}t$$

$$z = \frac{2kT}{F}\left(1 - e^{-\frac{F}{m}t}\right)$$

F is approximately given by Stokes's law, Eq. (3-5), and if this value of F is computed, using $a = 10^{-4}$ cm. and $\eta = 10^{-2}$ (which are of the proper order of magnitude), we have $F/m \cong 10^6$. Hence the exponential term in the above expression is negligible for times of observation longer than 10^{-5} sec. As the times used are generally of the order of 1 sec., we may write

$$z = \frac{d}{dt}\overline{x^2} = \frac{2kT}{F}$$

Integrating again, over the time interval τ during which the average squared displacement is $\overline{x^2}$, we obtain

$$\overline{x^2} = \frac{2kT\tau}{F} \tag{3-14}$$

or if Stokes's law is assumed to hold rigorously,

$$\overline{x^2} = \frac{kT\tau}{3\pi\eta a} = \frac{RT\tau}{3N\pi\eta a} \tag{3-15}$$

Thus the average squared displacement should be proportional to the absolute temperature and the time of observation, and inversely proportional to the viscosity of the suspending fluid and the radius of the particle. Perrin, in making his measurements, as we have indicated, showed that the average squared displacement did vary in the proper way with these factors. He also demonstrated that the squared displacements, measured in the time τ, were grouped about the average as would be expected if the displacements occurred at random. The table on page 95 shows the wide ranges of η and of a which were employed, and the values of N which were obtained.

These results demonstrate very conclusively the correctness of all the assumptions as to the mechanism of Brownian motion which were used in the derivation of Eq. (3-15). The values of N agree quite well among themselves and with the values obtained by Perrin from his observations on the numbers of particles found at different heights in a suspension.

The most accurate measurements on Brownian motion have been made by Fletcher[1] on the displacement of small spheres suspended in a gas. As this work depends on the technique involved in the measurement of the elementary electric charge, a description of the method will be deferred until after Millikan's procedure for measuring the charge of the electron has been described.

$\eta \times 10^2$	Emulsion	Radius $\times 10^4$ cm.	Mass $\times 10^{15}$ grams	Number of displacements	$N \times 10^{-23}$
1	Gamboge	0.5	600	100	8.0
1	Gamboge	0.212	48	900	6.95
4-5	Gamboge in 35 per cent sugar solution	0.212	48	400	5.5
1	Mastic	0.52	650	1,000	7.25
1.2	Large mastic in 27 per cent urea solution	5.5	750,000	100	7.8
125	Gamboge in glycerine with 10 per cent water	0.385	290	100	6.4
1	Gamboge of very uniform quality	0.367	246	1,500	6.88

3-5. The Atomic Nature of Electricity.—The conception of an elementary indivisible electric charge can hardly be said to have exercised a dominant influence on the development of electrical theory until the beginning of the twentieth century. The early "fluid" theories of electricity were based on the phenomena of the force of attraction between electric charges, which was measured by Coulomb in 1785, the flow of electricity along conductors, and the assumption, on rather inconclusive evidence, of the production of equal quantities of positive and negative charge whenever any electricity is generated. As their name implies, the fluid theories considered electricity as a continuous entity. However, Franklin, the leading exponent of the single-fluid theory, permitted himself certain speculations on the possibility of a "particle" concept of charge.

The first experimental evidence for the granular nature of electricity we owe to Faraday.[2] He found that in an electric circuit containing two solutions in series, say an acid and a base, equal quantities of hydrogen were generated per second at the two negative electrodes. Also, if a similar circuit was arranged in which one solution was an acid and the other a silver salt, the ratio of the weight of silver deposited on the negative electrode to the mass of hydrogen evolved in a given time was found to be 107.1:1. This was known to be the ratio of the atomic weights of silver and hydrogen. On the basis of such experiments performed with quite a large number of substances, Faraday announced his *laws of electrolysis*, which may be stated as follows:

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[1] Fletcher, *Phys. Rev.*, **33**, 81 (1911).

[2] Faraday, "Experimental Researches in Electricity," vol. I, p. 127 (1839).

1. The amount of an element deposited at an electrode in a cell is proportional to the quantity of electricity which has passed through the cell.

2. Equal amounts of electricity deposit equal numbers of gram-equivalents of different elements.

(A gram-equivalent is defined as a gram-molecule of an element divided by its valence.)

These laws suggest very strongly that there is a unit quantity of electricity associated with each univalent atom deposited in electrolysis, two units with each divalent atom, etc. The performance of such an electrolysis experiment is very simple and determines the product of the unit electric charge e and the number of molecules per gram-molecule, Avogadro's number N. On this hypothesis, a mass m' of a univalent element of atomic weight M is deposited by a current i flowing for a time t, and we have the following relation:

$$\frac{m'}{M} Ne = it$$

or

$$Ne = \frac{Mit}{m'} \tag{3-16}$$

The quantities on the right are all directly measurable by the experiment, except M, which we assume to be previously known. As an example, it is found that a unit current (in the electromagnetic system) flowing for 1 sec. deposits 0.0111805 gram of silver, for which M is 107.88, so that

$$Ne = \frac{107.88}{0.0111805} = 9{,}648.9 \text{ e.m.u. per gram-molecule}$$

This universal constant is known as the *faraday*. We may thus determine e to the accuracy with which N is known. The accuracy of Perrin's value for N is not great, but taking the extreme values from the previous table, we may say that e probably lies between 1.24×10^{-20} and 1.76×10^{-20} e.m.u. of charge, or between 3.62×10^{-10} and 5.28×10^{-10} e.s.u. (Fundamentally, this method of determining e is probably capable of great accuracy. N may be determined quite precisely by measuring the crystal diffraction of X-rays whose wave length has previously been measured with a ruled grating as described in Chap. IX. Work of this kind has been done recently by Bearden,[1] but the value obtained for e is not in good agreement with that found by the methods to be described later.)

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[1] Bearden, *Proc. Nat. Acad. Sci.*, **15**, 528 (1929); *Phys. Rev.*, **37**, 1210 (1931); **39**, 1 (1932).

Birge, *Phys. Rev. Suppl.* (*Rev. Mod. Phys.*), **1**, 40, 70 (1929).

The development of electrical theory, however, at the time of Faraday's work and for many years thereafter, was along mathematical lines, on the conception of electric forces as a strain in an all pervading medium known as the "ether." As a consequence, the implications of Faraday's laws were not realized nor were the calculations outlined in the preceding paragraph performed until a much later date. In 1874, C. Johnstone Stoney,[1] to whom we owe the name *electron* for the elementary negative charge, championed the cause of the atomic theory of electricity and actually estimated the size of the unit charge to be 0.3×10^{-10} e.s.u. At about the same time, Helmholtz saw the necessity for the atomic concept of electricity, on the evidence of Faraday's laws and the atomic theory of matter. Physicists during the nineteenth century had been greatly hampered in their speculations by the lack of accurate experimental data with which to test their ideas; it was not until exact measurements were available that the atomic theory of electricity took on a thoroughly convincing aspect.

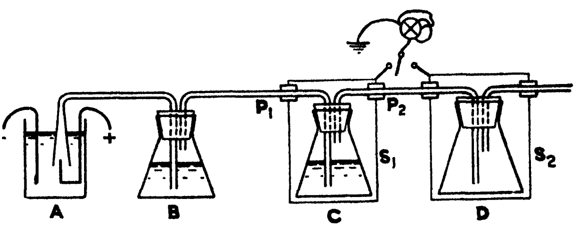

FIG. 3-3. Townsend's method of measuring e.

3-6. Measurement of the Electronic Charge by the Cloud Method.—

The first attempt to measure e directly was made by Townsend[2] in the Cavendish Laboratory at Cambridge, in 1897. The method was based on the tendency for charged particles to act as nuclei upon which condensation occurs in saturated vapors. The apparatus is shown schematically in Fig. 3-3.

The solution in A is electrolyzed by a heavy current and the oxygen generated at the positive electrode passes into the vessel B. This oxygen contains a large number of charged molecules carried out of the solution by the violence of the electrolysis. Any ozone in the gas is absorbed by the solution in B. A fine mist of water drops is formed on the ions in the saturated vapor in B, and this spray passes through the insulating plug P_1 into the drying agent in C. Here all the water drops are removed and part of the charge remains in C, thus inducing an equal charge on the

[1] STONEY, *Phil. Mag.*, **11**, 384 (1881).

[2] TOWNSEND, *Proc. Camb. Phil. Soc.*, **9**, 244 (1897).

outside of the shield S_1. The charge so acquired is measured with an electrometer. The dry gas leaving C passes into D where it is collected and a charge is induced on the shield S_2 equal to the charge carried into D; this charge is also measured.

The mass of a typical drop is determined by measuring its rate of fall under gravity and applying Stokes's law, by Eq. (3-7). If the weight gained by C in a given time is M', and the mass of an average drop is m', then the number of drops entering C is M'/m'. The sum of the charges E_1 on S_1 and E_2 on S_2 divided by the number of drops gives the charge per drop. The rather questionable assumption is made that one elementary unit charge e forms the nucleus of each drop, so that

$$e = (E_1 + E_2)\frac{m'}{M'} \tag{3-17}$$

Townsend obtained a value of about 3×10^{-10} e.s.u. for e.

Two other methods using clouds condensed on charged particles were developed by J. J. Thomson[1] and by H. A. Wilson.[2] The procedures were slightly more precise, the values obtained being 3.4×10^{-10} and 3.1×10^{-10} e.s.u. respectively. These cloud methods, at best, can determine e only as an average value; measurements on individual charges were first obtained by Millikan.

3-7. Measurement of the Electronic Charge by the Oil-drop Method. Millikan[3] in 1909 devised a method of measuring e with great accuracy. A minute charged drop of a liquid is placed between two horizontal condenser plates, and its velocity of fall under gravity and its velocity of rise under an applied electric field are measured. From these data the charge on the drop may be calculated, as will be shown. If ions are present in the region between the plates, some of them may come in contact with the drop and its charge will be altered. These changes in charge may be measured by further observations on the velocities, and it is found that all the changes are integral multiples of a smallest charge which is therefore undoubtedly the fundamental natural unit e.

The equation of motion of a particle of mass m acted on by an accelerating force X along the x-axis and by a retarding force proportional to its velocity is

$$m\frac{d^2x}{dt^2} = -F\frac{dx}{dt} + X \tag{3-18}$$

where F is the constant of proportionality of the retarding force. When the motion has reached a steady state, *i.e.*, when the acceleration is zero, we have

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[1] THOMSON, J. J., *Phil. Mag.*, **46**, 528 (1898).

[2] WILSON, H. A., *Phil. Mag.*, **5**, 429 (1903).

[3] MILLIKAN, "The Electron," University Chicago Press (1927). *Phys. Rev.*, **29**, 560 (1909); **32**, 349 (1911); **2**, 109 (1913). *Phil. Mag.*, **19**, 209 (1910); **34**, 1 (1917).

$$\frac{dx}{dt} = \frac{X}{F}$$

Thus this terminal velocity is proportional to the applied force X. If the particle is falling under gravity, its velocity is therefore given by

$$v_g = \frac{m'g}{F} \tag{3-19}$$

where $m'g$ is the downward force of gravity diminished by the buoyant force of the medium displaced by the particle, the effective mass m' being equal to $m\left(\frac{\rho - \sigma}{\rho}\right)$, with ρ the density of the particle and σ that of the medium. When the particle is rising under the influence of an electric field, E e.s.u., we have

$$v_E = \frac{Ee_n - m'g}{F} \tag{3-20}$$

where e_n is the number of unit charges on the particle. (We have taken each velocity to be a positive quantity.) Taking the ratio of these last two equations and solving for e_n, we obtain

$$e_n = \frac{m'g}{E}\left(\frac{v_E + v_g}{v_g}\right)$$

or

$$e_n = m\left(\frac{\rho - \sigma}{\rho}\right)\frac{g}{E}\left(\frac{v_E + v_g}{v_g}\right)$$

We may write for E its value V/d where V is the potential difference in electrostatic units between the condenser plates, and d is their separation in centimeters. Assuming the validity of Stokes's law, we may express m in the form given by Eq. (3-7), and thus obtain

$$e_n = \frac{4}{3}\pi\left(\frac{9}{2}\eta\right)^{\frac{3}{2}}\frac{d}{V}\left(\frac{1}{(\rho - \sigma)g}\right)^{\frac{1}{2}}(v_E + v_g)v_g^{\frac{1}{2}} \tag{3-21}$$

Hence the charge e_n may be calculated if the other quantities are known If the atomic conception of electricity is correct, the total charge on the particle is always an integral multiple of the unit charge, and any changes in charge, due to collisions with ions, must also occur in units. The quantity $(v_E + v_g)$ is equivalent to the velocity the particle would have in a purely electric field undiminished by gravity and hence is directly proportional to the force on the particle in such a situation; *i.e.*, it is proportional to the total charge on the particle, if the electric field remains constant. Therefore it should be possible to find a greatest common divisor $(v_E + v_g)_1$ of the various values of $(v_E + v_g)$ that are observed as the charge on the particle changes. The quantity $(v_E + v_g)_1$ is hence directly proportional to the unit charge which may be found from the expression

$$e_1 = \frac{4}{3}\pi\left(\frac{9}{2}\eta\right)^{\frac{3}{2}} \frac{d}{V}\left(\frac{1}{(\rho - \sigma)g}\right)^{\frac{1}{2}} (v_E + v_g)_1 v_g^{\frac{1}{2}} \tag{3-22}$$

Not only can one thus determine, essentially, e_1 as being the greatest common divisor of the various total charges e_n, but e_1 may also be found from the successive changes in the value of e_n. If v_E and v_E' are successive values of the velocity when the charge changes, then $v_E - v_E'$ is proportional to the change in charge; the smallest value of this difference is then proportional to the unit charge. (In a long series of observations it is almost certain that at least once the charge will change by only one unit.) We have then

$$e_1 = \frac{4}{3}\pi\left(\frac{9}{2}\eta\right)^{\frac{3}{2}} \frac{d}{V}\left(\frac{1}{(\rho - \sigma)g}\right)^{\frac{1}{2}} (v_E - v_E')_1 v_g^{\frac{1}{2}} \tag{3-23}$$

These equations were tested by Millikan and found to yield consistent results only for drops falling with the same velocities. This discrepancy was traced to a failure of Stokes's law for drops of the dimensions used.

3-8. Correction to Stokes's Law.—One of the assumptions involved in the derivation of Stokes's law is that the sizes of the inhomogeneities in the fluid are negligible compared to the dimensions of the moving sphere. If n is the number of molecules of the fluid per unit volume, $1/n$ is the volume occupied by one molecule. Also, if a is the radius of the drop, we may take c/na, where c is a constant, as measuring the ratio of the volume per molecule of fluid to the size of the sphere; therefore, c/na is a measure of the inhomogeneity of the fluid. This quantity is small for the size of drop used, but it is evidently not completely negligible. The difference between the Stokes velocity and the observed velocity is some function of c/na that vanishes when c/na vanishes, so if c/na is sufficiently small we may say, to a first approximation, that the difference between the observed and calculated velocities is the first term of a power series in c/na, or simply a constant, say A/c, multiplied by c/na; *i.e.*,

$$v_{\text{obs.}} = v_{\text{calc.}} + \frac{A}{na}$$

Since n is directly proportional to the pressure, we may replace A/na by $v_{\text{calc.}}b/pa$ where b is some other constant. For $v_{\text{calc.}}$ we may use the value of v given by Stokes's law, through Eq. (3-6), thus obtaining

$$v_{\text{obs.}} = \frac{2g}{9\eta}a^2(\rho - \sigma)\left(1 + \frac{b}{pa}\right)$$

This shows that if we wish to correct for the failure of Stokes's law, we should multiply the calculated velocity by the factor $\left(1 + \frac{b}{pa}\right)$. Since the equation for the unit charge contains the velocity to the

$\frac{3}{2}$ power, we may evidently write for the true unit charge, to this degree of approximation,

$$e = \frac{e_1}{\left(1 + \frac{b}{pa}\right)^{\frac{3}{2}}} \tag{3-24}$$

The radius of the drop a enters in the small correction term, so that a may be obtained with sufficient precision by solving the uncorrected Stokes's expression Eq. (3-6). The pressure may be observed and e_1 calculated from Eq. (3-22) or (3-23). The same procedure may be used for a second drop and, from the two equations so obtained, e and b may be determined. However, to insure that the reasoning in developing Eq. (3-24) is correct, as large a number of drops as possible should be investigated in order to confirm the constancy of the values of e and b.

Millikan verified Eq. (3-24) conclusively by a long series of very accurate measurements. If p was measured in centimeters of mercury at 23°C. and a in centimeters, the value of b was found to be

$$b = 0.000617$$

The value for the viscosity constant of air, at this temperature, was taken as

$$\eta_{23} = 0.00018226$$

The description of the apparatus, method of observation, and the precautions taken are given in Millikan's book, "The Electron." The final value obtained for the elementary natural unit of charge was

$$e = (4.774 \pm 0.005) \times 10^{-10} \text{ e.s.u.}$$

3-9. Measurement of the Electronic Charge by the Shot Effect.—There is one other direct method of measuring e which is worthy of brief mention. In the phenomenon of thermionic emission, which will be discussed in greater detail in Chap. VI, it is observed that a wire maintained at a high temperature emits negative electricity. That is, if such a wire be surrounded by a metallic cylinder kept at a positive potential with respect to the wire, an electric current flows between the wire and the cylinder. If the region inside the cylinder is evacuated, the complicating effects of the gas are removed. If the current consists of discrete negative charges of magnitude e emitted by the hot wire, this current will not be steady but will be the sum of the minute charges given up by each electron as it strikes the cylinder. These electrical impulses may be used to set up oscillations, in an external resonating circuit of inductance and capacity in parallel, by the method of shock excitation. These oscillations may be amplified and measured. Schottky[1] has shown from statistical considerations that if the potential on the collecting cylinder is sufficiently high to collect all the electrons leaving the wire, the value of the charge on the electron is given by

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[1] SCHOTTKY, *Phys. Rev.*, **28**, 74, 1331 (1926); and references there cited.

$$e = \frac{2RC\Delta\bar{I}^2}{i}$$

where R is the resistance of the inductance, C is the capacity, i is the current flowing in the circuit, and $\Delta\bar{I}^2$ is the mean squared value of the current fluctuations in the oscillating circuit. The theory involved is not simple and the experimental measurements are difficult. The natural frequency of the oscillating circuit must be high (of the order of hundreds of kilocycles per second) or disturbances will be present which will mask the effect sought for. Hull and Williams,[1] with an apparatus indicated in Fig. 3-4, obtained a value for e of 4.76×10^{-10} e.s.u., with a probable error considerably larger than that in Millikan's work.

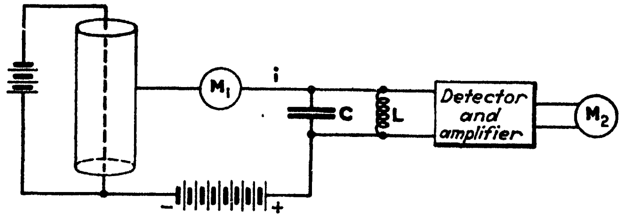

FIG. 3-4.—The method of Hull and Williams for the measurement of e, using the shot effect.

3-10. Oil-drop Experiment.—An apparatus for measuring the charge of the electron by the oil-drop method may be purchased, or it may be constructed very simply.[2] An apparatus designed for measuring both e by the drop method and N by the Brownian motion in gases is shown in Figs. 3-5 and 3-6. As the Brownian motion has a larger amplitude at low pressures, and hence is more easily measured, the apparatus is built in such a way that it can be evacuated.

The two plates P_1 and P_2 are of brass, 10 cm. in diameter and 0.4 cm. thick. The inner faces are turned accurately flat. They are mounted in the hard-rubber cylinder A and are separated by a ridge 0.7 cm. thick turned in the cylinder. The smaller this separation, the lower is the potential that may be used satisfactorily; but if the separation is too small, the manipulation of the drops becomes difficult. Four holes 1 cm. in diameter are cut through the cylinder; two are for illumination of the space between the plates, a third for observation, and the fourth for admitting ionizing particles from the radioactive source R. These holes are covered with sheets of cellophane cemented in place to prevent gas currents outside the plates from disturbing the motion of the drops. Holes are also drilled through the cylinder below P_1, so that pressure equilibrium may be readily established in that region. A helical spring soldered to P_1 makes electrical contact with the bottom of the enclosing vessel.

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[1] HULL and WILLIAMS, *Phys. Rev.*, **25**, 148 (1925).

[2] HOAG, "Electron Physics," Van Nostrand (1929).

The upper plate P_2 has a No. 60 hole drilled through its center to admit the oil drops. A flat iron bar S, $\frac{1}{8}$ by $\frac{3}{8}$ by 5 in., with a No. 54 hole in its center, slides lengthwise on a diameter of P_2, the motion being limited by pins in the plate engaging slots in the bar, in such a way that in one of the extreme positions the two holes are in line. The motion of the bar is caused by external electromagnets, so that a convenient shutter is formed to prohibit the entrance of more oil drops into the space between the plates after a satisfactory drop has been found. A wire soldered to P_2 passes out of the vessel through the bakelite plug in the lid, a spring clip connector being included in the wire to permit removal of the lid.

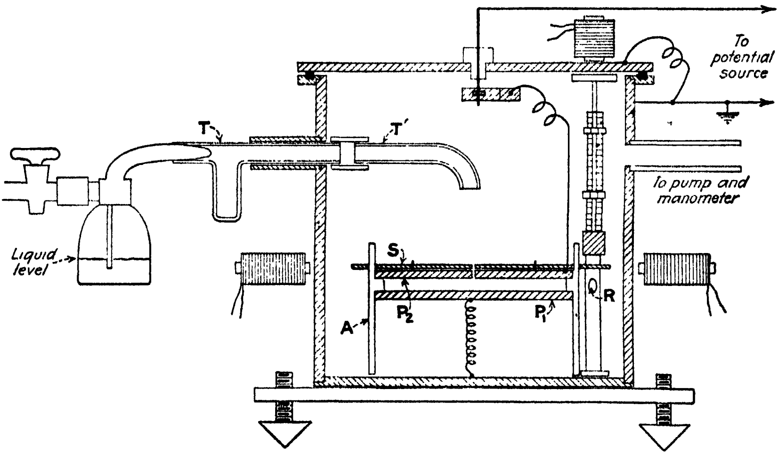

FIG. 3-5.—Millikan oil-drop apparatus for measuring the charge of an electron.

The containing vessel itself is a brass pot supported by three leveling screws. The walls are made of a 6-in. length of $\frac{1}{8}$-in. brass tubing 6 in. in diameter. The top and bottom are of $\frac{1}{4}$-in. rolled brass plate. A flange is soldered around the top of the cylinder, and a greased rubber gasket, lying in a circular groove in the flange, renders the lid vacuum tight. If the surfaces are ground together and greased, the gasket may be dispensed with. Two cylindrical brass tubes, the external ends of each covered with glass windows waxed in place, are soldered into the pot for illumination and observation, as shown in Fig. 3-6. Two smaller brass pipes are also provided, one for connection to the pump and manometer and the other for the admission of the oil spray from an ordinary medical atomizer. The latter is waxed to make it vacuum tight, and connected to the brass tube *via* a glass pipe T containing a small appendix to collect excess oil. A second tube T', attached with a rubber coupling, directs the oil spray toward the hole in P_2. A stopcock on the intake of the atomizer admits a blast of air or hydrogen when opened.

The radioactive source, such as polonium or a radium salt, for the production of ions in the region between the plates, is located at R (Fig. 3-5). The material is placed in a vertical lead tube pierced with a hole at the level of the space between the plates. A rod, sliding vertically in guides on the tube, carries at its lower end a lead shutter which covers the hole when the rod is in its lowest position. On the upper end of the rod is a piece of iron so that the shutter can be lifted and the source uncovered by energizing an electromagnet placed on the lid of the pot above the iron armature. This arrangement has been found more satisfactory than having the ionizing agent outside of the vessel, as the ionization is much more intense and a change in charge can be produced in a very short time; this is sometimes necessary if the drop happens to become completely uncharged.

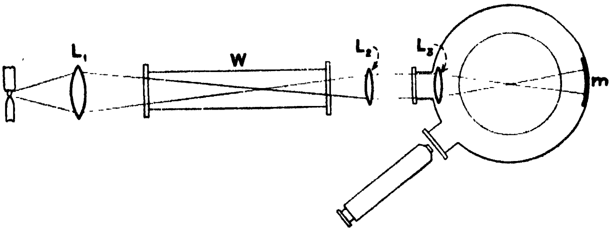

FIG. 3-6.—An illumination system for the Millikan oil-drop experiment.

The illuminating system is shown in Fig. 3-6. Light from an arc or Point-o-lite lamp is condensed by the lens L_1 and is passed through the water cell W, which removes most of the energy in the infra-red region of the spectrum. This materially decreases the heating of the plates and the gas between them and so reduces the disturbing effect of convection currents. The light converges at the principal focus of L_2, from which it proceeds into the chamber and through L_3; this brings it to a focus immediately below the hole in the upper plate. A mirror m, with a radius of curvature equal to the radius of the chamber, is placed as shown in the figure and reflects the light back to the center. This greatly increases the illumination of the oil drops.

The observations are made with a microscope of about 8-cm. focal length and a rather deep field. The measurements to determine e are made with a ruled scale at the focus of the eyepiece; the time of passage of an oil drop over some standard interval is determined with a stop watch. This interval is translated into centimeters by placing a standard scale at the focus of the microscope and comparing the eyepiece intervals with those of the standard scale. Brownian motion measurements may be made with such a scale turned with the rulings in a vertical position or with a microscope equipped with cross hairs carried by a micrometer screw.

Many arrangements alternative to those described above may be used satisfactorily. The description has been given in detail merely to afford suggestions for the construction of an apparatus to fullfil similar functions.

The most convenient source of potential is a battery or generator, but the arrangement shown in Fig. 3-7 is quite satisfactory. The secondary of the transformer T, supplying about 1,500 or 2,000 volts, is connected in series with the rectifying tube K (which need not be large) and the condenser C. This should have a capacity of about 1 μf. and should be capable of withstanding the peak voltage. Protective resistances R_1 and R_2, of about 50,000 ohms each, connect the condenser terminals to a good high-resistance or electrostatic voltmeter V and the reversing switch. These resistances protect the operator and also the apparatus in case of a short circuit. The wire going to the pot and the lower plate P_1 should be grounded, and also connected to the lid if the rubber gasket is used. The grounding of the plate P_2 may be effected by a spring contact across the arms of the reversing switch that short-circuits them when the handle is in the neutral position, or by a resistance R_3 of several megohms permanently placed across the wires to the plates, as shown in the figure. The switch should be guarded in such a way that only the handle can be touched by the operator, whose attention is on the oil drop.

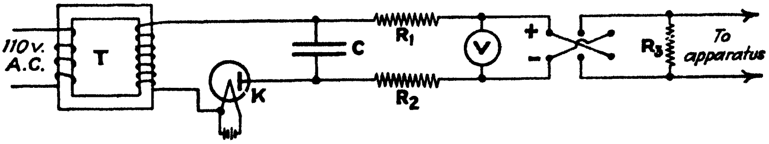

FIG. 3-7.—A transformer and rectifier potential source for the Millikan oil-drop determination of *e*.

Any value of the potential, between that which will just support a drop, carrying one unit charge, against gravity and the potential which will cause a disruptive discharge, is satisfactory. A convenient-sized drop is one which falls under gravity at about 0.01 cm. per second. Such a drop can be seen easily, and its velocity accurately measured. The radius is about 10^{-4} cm. and the mass approximately 2×10^{-12} gram, so that with unit charge a field of about 4 e.s.u. will support it. With a plate separation of 0.7 cm., this corresponds to 840 volts. A larger potential is more convenient; although a smaller one can be used, there is then a greater chance of losing the drop.

The most satisfactory liquid from which to produce the drops is a high grade of clock oil. It works readily in an ordinary atomizer and its rate of evaporation is so slow that the same drop may be used for several hours with only a small change in mass. When properly illuminated, the drops appear as very bright points of light against a black background.

It is essential that the plates be accurately level as otherwise the gravitational and electric fields are not parallel and the drops soon drift out of the field of view. Preliminary adjustments may be made with a spirit level and final adjustment from the behavior of a drop. A wire thrust through the hole in the upper plate is convenient for initially focusing the microscope. In determining the value of e it is not necessary to evacuate the chamber, and the atomizer therefore may be operated with a rubber bulb in the usual manner. When drops appear in the field of view, a few rapid throws of the switch will show which ones have been frictionally charged on leaving the atomizer and one may be chosen that has a convenient rate of fall under gravity. The shutter over the oil hole is then closed, and judicious throws of the switch will soon clear the field of all but the chosen drop. The actual timing of the velocities of rise with the field, and of fall with gravity, may then be started. It is advisable for one person to control the drop and handle the stop watch while an assistant reads the watch and records the data. To insure the applicability of the fundamental assumption of steady velocity, the drop should be allowed to move some distance before timing is started. After several successive times of rise under the electric field have been obtained that agree with each other to within the accuracy of timing, the shutter covering the radioactive source may be opened to give the drop an opportunity to change its charge by collision with the ions formed by the rays emitted from the source. Another series of observations is then made with the new charge. Ten or twenty changes of charge should be observed for accurate results. Times of fall over the same standard distance under gravity should be recorded from time to time during the experiment. Irregular motion of the drops is generally due to the temperature between the plates not having reached a steady state or to incorrect leveling of the apparatus. Occasionally a drop may be observed to alter its charge during its motion under the field; such an observation is, of course, not included in the data.

The observations may be most conveniently analyzed in the tabular form shown for the sample data given in the accompanying table. It is simpler to deal with reciprocal times in the early stages of the calculations than with the velocities to which they are proportional. Since $(v_E + v_G)_1$ and $(v_E - v_E')_1$ occur symmetrically in Eqs. (3-22) and (3-23), one may take the average value of these two quantities and use this average in either of the equations which are then identical. The oil density ρ may be found by a simple auxiliary experiment, and the values of η, σ, and g may be obtained from tables of physical constants or measured experimentally. Values of e agreeing to within 1 or 2 per cent with the accepted value may easily be obtained.

SAMPLE DATA OF OIL-DROP METHOD OF DETERMINING *e*

t_g	t_E	Mean t_E	$\frac{1}{t_E}$	$\left(\frac{1}{t_E}-\frac{1}{t_E'}\right)$	n'	$\frac{1}{n'}\left(\frac{1}{t_E}-\frac{1}{t_E'}\right)$	$\left(\frac{1}{t_E}+\frac{1}{t_g}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_E}+\frac{1}{t_g}\right)$
12.65	3.00	3.00	0.333				0.411	8	0.051
13.01	4.46			0.106	2	0.053			
	4.36								
12.79	4.40	4.40	0.228				0.306	6	0.051
	4.42			0.049	1	0.049			
13.25	5.66								
	5.50	5.58	0.179				0.257	5	0.051
12.53	5.58			0.059	1	0.059			
	4.14								
12.94	4.22	4.21	0.238				0.316	6	0.053
	4.28			0.051	1	0.051			
12.63	5.32								
	5.32	5.35	0.187				0.265	5	0.053
13.15	5.42			0.055	1	0.055			
	7.58								
13.27	7.62	7.55	0.132				0.201	4	0.052
	7.46			0.051	1	0.051			
12.55	12.36								
	12.36	12.33	0.081				0.159	3	0.053
12.90	12.28			0.151	3	0.050			
	4.14								
12.84	4.42	4.32	0.232				0.310	6	0.052
	4.42								
13.17	4.28			0.149	3	0.050			
	12.04								
13.10	11.90	12.03	0.083				0.161	3	0.054
	12.50								
12.92	11.98			0.053	1	0.053			
	33.66								
12.70	33.12	32.89	0.030				0.108	2	0.054
12.50	33.10								
12.55	32.70								
12.858 mean						0.0523 mean			0.0524 mean

Fall distance = 0.180 cm. $T = 23°\text{C}.$ $b = 0.000617$

$\eta = 0.0001823$ $\rho = 0.899$ $V = 1{,}500$ volts

$g = 981$ $\sigma = 0.001$ Mean of $\frac{1}{t_g} = 0.078$

$p = 76.00$ cm. Hg $d = 0.70$ cm. Mean of columns 7 and 10 = 0.05235

$v_g = 0.078 \times 0.180 = 0.01384$ cm. sec.$^{-1}$ $(v_E + v_g)_1 = 0.05235 \times 0.180 = 0.00942$ cm. sec.$^{-1}$. $e_1 = 5.18 \times 10^{-10}$ e.s.u. $e = 4.67 \times 10^{-10}$ e.s.u.

3-11. Determination of Avogadro's Number from Brownian Motion. In the course of observations on the oil drops when measuring the charge of the electron, the irregular Brownian motion of the drops will doubtless have been observed. The displacements can be rendered much more pronounced if the apparatus is evacuated. By Eq. (3-14) we see that this is due to a decrease in the retarding force of the medium, which may be pictured as a reduction in the density of gas molecules through which the drop must force its way. Since it is known that the viscosity η does not vary with the pressure, it is evident that Eq. (3-15) is not applicable; the increased motion must be ascribed to a greater failure of Stokes's law than occurs at the higher pressures used in measuring e. The frictional force F still varies with the viscosity, since if hydrogen is used, which has a viscosity about half that of air, the displacements are doubled in magnitude, but the form of the relation cannot be the simple one given by Stokes.

We are able, however, to obtain a numerical measure of the value of F without regard to any theoretical form of the function, provided we make the assumption that the frictional force is proportional to the velocity, even at low pressures. · This assumption is justified by the results. On this basis we have from Eq. (3-19)

$$F = \frac{m'g}{v_g}$$

and from Eq. (3-20)

$$m'g = \frac{eEv_g}{(v_E + v_g)_1}$$

where we have taken unit charge and the corresponding value of $(v_E + v_g)$, as determined by a series of measurements with different charges. From these two equations we obtain

$$F = \frac{eE}{(v_E + v_g)_1} \tag{3-25}$$

so that the truth or falseness of Stokes's law need not concern us. Eliminating F between Eqs. (3-14) and (3-25), and setting $k = R/N$, we find

$$\overline{x^2} = \frac{2RT\tau(v_E + v_g)_1}{NeE}$$

or

$$Ne = \frac{2RT\tau(v_E + v_g)_1}{E\overline{x^2}} \tag{3-26}$$

Thus, measurements of the velocities of the oil drop when rising and falling under the electric field and gravity, followed by observations on the horizontal Brownian displacements when the electric field has been adjusted to exactly support the particle against gravity, suffice to determine the product Ne, since the gas constant R, the absolute temperature, and the electric field strength are known. With the charge e known from Millikan's method, we may calculate Avogadro's number N.

The above expression, however, involves the laborious process of squaring each of the several hundred individual displacements and then taking their average. A relation between the much more easily found quantity $(\bar{x})^2$ and $\overline{x^2}$ may be determined by the following considerations.

As is shown in books on the theory of probability, if a series of measurements, each subject to random accidental errors, is made on any quantity, the probability of making an error x is given by $P(x)dx$, where

$$P(x)dx = \frac{he^{-h^2x^2}}{\sqrt{\pi}}\,dx \tag{3-27}$$

where h is a constant that depends on the precision with which the measurements can be made. It has been experimentally demonstrated that this expression represents very accurately the deviations from the mean value in many types of random distributions. Hence if the Brownian motions are themselves perfectly random, as we have assumed, they should obey this law. The average of the square of the displacements, $\overline{x^2}$, is then the integral from $-\infty$ to $+\infty$ of x^2 multiplied by the probability that x should occur; *i.e.*,

$$\overline{x^2} = \int_{-\infty}^{\infty} x^2P(x)dx = 2\int_0^{\infty} x^2P(x)dx = \frac{2h}{\sqrt{\pi}}\int_0^{\infty} x^2e^{-h^2x^2}dx = \frac{2h}{\sqrt{\pi}}\frac{\sqrt{\pi}}{4h^3} = \frac{1}{2h^2}$$

as may be found in tables of integrals. Hence $h = 1/\sqrt{2\overline{x^2}}$, and we may write Eq. (3-27) in the form

$$P(x)dx = \frac{1}{\sqrt{2\pi}\sqrt{\overline{x^2}}}e^{-\frac{x^2}{2\overline{x^2}}}\,dx \tag{3-28}$$

We may now use this expression to find the average value of x, in terms of $\overline{x^2}$, for $\bar{x}$ is twice the integral from 0 to ∞ of x multiplied by the probability of x; thus

$$\bar{x} = 2\int_0^{\infty} xP(x)dx = \frac{2}{\sqrt{2\pi}\sqrt{\overline{x^2}}}\int_0^{\infty} xe^{-\frac{x^2}{2\overline{x^2}}}dx$$

Using the substitution, $z = x^2/2\overline{x^2}$, so that $2xdx = 2\overline{x^2}\,dz$, this is

$$\bar{x} = \frac{2\overline{x^2}}{\sqrt{2\pi}\sqrt{\overline{x^2}}}\int_0^{\infty} e^{-z}\,dz = \frac{\sqrt{2}}{\sqrt{\pi}}\sqrt{\overline{x^2}}$$

Therefore

$$\overline{x^2} = \frac{\pi}{2}(\bar{x})^2 \tag{3-29}$$

Using this with Eq. (3-26) and setting $E = V/d$, where d is the separation of the plates in centimeters, and V is the potential difference between

them in electrostatic units when the quantity $(v_E + v_g)_1$ is being determined, we obtain

$$Ne = \frac{4RT\tau d(v_E + v_g)_1}{\pi V(\bar{x})^2} \qquad (3\text{-}30)$$

The gas pressure to be used in the apparatus is not critical, but if it is too low the electric field may produce some ionization by the acceleration of ions in the region between the plates, thus causing the conditions to become very unsteady. A high resistance should be connected in series with the potential source to prevent an arc from striking. A pressure of a few centimeters of mercury has been found very satisfactory. The field is applied to the plates by a high-resistance potentiometer across the generator or battery, or if the transformer and rectifier circuit is used, a rheostat is placed in the primary circuit of the transformer, so that the chosen drop may be balanced against gravity by adjusting the electric field.

It is wise to determine first the quantity $(v_E + v_g)_1$ or $(v_E - v_E')_1$, by changing the charge of the drop several times by means of the radioactive source and noting the potential used, as though the charge e were to be found. Then the potential is varied until the drop is balanced against gravity, and the horizontal Brownian displacements of the same drop are measured. (This order of procedure permits the use of all data taken up to the time the drop is lost.) The scale in the eyepiece of the microscope is turned into a horizontal position and estimates are made of the position of the drop at the beginning and end of some suitable time interval, say ten seconds. If the scale is not numbered, it is perhaps easier for the observer to call out each horizontal motion of the drop, such as "one right, two left"; these data are recorded by an assistant who notes also the time intervals. An alternative arrangement is to replace the eyepiece and scale by an eyepiece containing a cross hair carried by a micrometer screw; the hair may be set on the drop every 10 sec. and the drum readings recorded. In case the drop should change its charge during the measurements, it is only necessary to alter the potential until the drop is again balanced; the potential applied during the Brownian measurements does not enter into the calculations. Observations may be made even with the drop moving slowly up or down, provided the scale divisions are accurately vertical. One or two hundred displacements will generally give a value for Ne, agreeing to within a few per cent of the accepted one.

A representative condensed set of data is shown in the following table and Fig. 3-8. The solid curve in the figure is a plot of

$$P(x') = \frac{1}{\pi\bar{x}'} e^{-\frac{x'^2}{\pi(\bar{x}')^2}}$$

which is obtained from Eq. (3-28) by means of Eq. (3-29). Here the displacement x' is measured in arbitrary scale units. The points in the figure represent the percentages of all the displacements that lie within unit range of a given value. It is seen that even with the few observations taken, the distribution of the displacements is sufficiently in agreement with the theoretical curve to justify our assumptions as to the randomness of the Brownian motion.

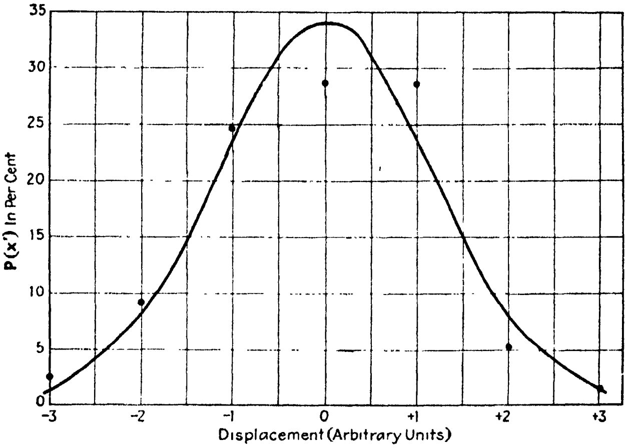

FIG. 3-8.—A graph showing the distribution of the net horizontal Brownian displacements of the oil drop during the 77 ten-second intervals as given in the accompanying table. Each point represents the percentage of all the displacements that lay within a range equal to the smallest distance that could be estimated (1 scale unit). The solid curve is a plot of the normal random distribution law.

TYPICAL BROWNIAN MOTION DATA

Of 77 ten-second intervals, the net motion of the drop was:

For 1.3 per cent of them, +3 units
For 5.2 per cent of them, +2 units
For 28.6 per cent of them, +1 unit
For 28.6 per cent of them, 0 unit
For 24.6 per cent of them, −1 unit
For 9.1 per cent of them, −2 units
For 2.6 per cent of them, −3 units

1 unit $= 2.85 \times 10^{-3}$ cm. $R = 8.314 \times 10^{7}$ ergs · deg.$^{-1}$
$\bar{x} = 0.9350$ unit $= 2.665 \times 10^{-3}$ cm. $T = 300°$ abs.
$V = 940$ volts $(v_E + v_g)_1 = 0.02685$ cm. sec.$^{-1}$
$d = 0.7$ cm. $\tau = 10$ sec.
$p = 8.3$ cm. of Hg (air)

Hence by Eq. (3-30),

$$Ne = 2.680 \times 10^{14} \text{ e.s.u. (gram-mol)}^{-1}$$

(Accepted value $= 2.8927 \times 10^{14}$)

Taking $e = 4.770 \times 10^{-10}$ e.s.u. we find

$$N = 5.62 \times 10^{23} \text{ (gram-mol)}^{-1}$$

(Accepted value $= 6.064 \times 10^{23}$)

CHAPTER IV

THE RATIO OF CHARGE TO MASS OF ELECTRONS AND OF IONS

4-1. Introduction.—If a metal is heated, the application of a small electric field will cause a current of negative electricity to flow from its surface. If the metal is not heated but a sufficiently large field be applied, of the order of 1,000,000 volts per centimeter, a negative current may be drawn from the metal. This current, as shown by the experiments of Schottky, and of Hull and Williams, which were briefly described in Chap. III, is borne by a stream of particles each carrying a negative charge of 4.77×10^{-10} c.s.u. These same particles may be liberated from a metal surface by the influence of radiation. That they are not a particular characteristic of metal surfaces may be shown by their appearance in the body of a gas subjected to heat, radiation, or an electric discharge. Finally, certain materials, known as radioactive substances, spontaneously emit these negatively charged particles.

By a number of methods which will be briefly described, these particles, or electrons, are all found to bear the same ratio of charge to mass, with the exception of those traveling at high speeds, when the apparent discrepancy can be explained by the relativistic change in mass. As their physical properties depend almost entirely upon their charge and mass, it is a reasonable conclusion that electrons are all exactly the same, from whatever source they may be obtained. Atomic theory postulates that electrons are universal constituents of all matter, and that, together with positively charged particles known as *protons*, they actually constitute all atoms.

The mass of one of these particles is so small that its direct measurement presents the greatest difficulties. The mass of an atom may be measured directly from the experimentally determined number in, say, a unit volume of a gas and the measured mass of that volume. An obvious analogy to this, in an effort to measure the mass of an electron, is to attempt to detect the difference in weight of a body of known capacity before and after charging it to a known potential. If a metal sphere, 1 meter in radius, were charged to a potential of 3,000,000 volts, the charge on it would be 10^6 e.s.u., which corresponds to about 2×10^{15} electrons. Indirect methods show that the mass of one electron is of the order of 10^{-27} gram, so that the sphere would increase in mass by only 2×10^{-12} gram, which is too small to be detected. As another attempt, we might suppose that, from the observation of a collision between an atom and an electron, we might apply the classical laws of mechanics, and, by a measurement of momentum transfer, calculate the mass of the electron. The mass of an atom is so much greater than that of an electron, that with the present available precision such a method is out of the question. Such a possibility does exist, however, in the interaction process between radiation and an electron. If the particle concept of radiation, mentioned in Chap. I and brought out experimentally in the photoelectric effect, is adopted, the classical laws of mechanics appear to be applicable to the collision of an X-ray particle or photon and an electron. Here the effective masses are of the same order of magnitude. As will be further discussed in connection with X-rays, such collisions, which give rise to the Compton effect, actually provide a method of measuring directly the mass of an electron.[1]

There are indirect methods of measuring this quantity which are of the greatest importance. Since we know the charge carried by each electron, if we are able to measure the ratio of the charge to the mass, we may calculate the mass. These indirect methods, which will now be discussed, are the more important because in many physical phenomena it is this ratio, e/m, that appears in the calculations, rather than either the charge or the mass separately. Thus, to a first approximation, the classical and quantum theories of the radiation from an atomic system in a magnetic field both predict that certain components of the spectral lines emitted should differ in frequency by the amount

$$\Delta\nu = \frac{e}{m}\frac{H}{4\pi}$$

where e is the charge in electromagnetic units and H is the magnetic field strength. Hence, if the values of all these quantities are known, the predicted frequency difference may be compared with that experimentally observed. An agreement constitutes a partial verification of the theory of the emission of radiation. Conversely, if the theory is substantiated by other experiments, the agreement between the predicted and observed frequency difference may be taken as evidence that the ratio e/m for an electron inside an atom is the same as that observed in experiments on free electrons.

4-2. The Equations of Motion of a Charged Particle.—The force in dynes on a charge $+e$ e.m.u. in an electric field of strength E e.m.u. is eE. By Ampere's law, the force per unit length on a wire carrying a current i e.m.u. in a magnetic field of strength H e.m.u. is equal to $iH \sin\theta$, where θ is the angle between the magnetic field and the current. This force is perpendicular to both the current and the magnetic field and is in such a direction that if the current flows in a positive direction along the x-axis, in Fig. 4-1, and if the magnetic field is along the positive y-axis, the motion will be in the direction of increasing z. The current i is the rate of transfer of charge, so if the current is composed of e e.m.u. of charge moving with a velocity v, the current in electromagnetic units is ev, and the force acting on it is evH_p, where H_p is the component of the magnetic field, in electromagnetic units, perpendicular to the motion v. Hence, if we have a particle with charge e moving with velocity components v_x, v_y, v_z in an electric and a magnetic field, the x component of the force on the charge is

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[1] SHARP, *Phys. Rev.*, **26**, 691 (1925).

$$F_x = eE_x + e(v_yH_z - v_zH_y)$$

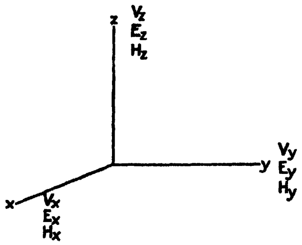

FIG. 4-1.—A right-hand coordinate system for discussing the motion of electrified particles.

The force is equal to the rate of change of momentum, so if the mass of the particle is m, we may write the three equations of motion as:

$$\frac{d(mv_x)}{dt} = eE_x + e(v_yH_z - v_zH_y) \tag{4-1}$$

$$\frac{d(mv_y)}{dt} = eE_y + e(v_zH_x - v_xH_z) \tag{4-2}$$

$$\frac{d(mv_z)}{dt} = eE_z + e(v_xH_y - v_yH_x) \tag{4-3}$$

These equations accurately represent the motion of a charged particle if the velocity is so small that terms of the magnitude of v^2/c^2, where c is the velocity of light, may be neglected. Only in the case of very high velocities, where the theory of relativity would essentially alter the result, is it necessary to consider that the mass is not constant. This will be discussed in the case of β rays, which are very high speed electrons emitted by radioactive materials. In the following discussion, the mass will be taken as constant. These strictly classical equations lead to the same predictions as the analogous equations based on quantum mechanics, which are here omitted. A treatment from this alternative standpoint may be found in any treatise on quantum mechanics.

4-3. *e/m* of Cathode Rays: Thomson's Method.—In 1897, Sir J. J. Thomson,[1] during his investigations of the phenomena connected with electrical discharges in gases, made the first measurements on e/m of electrons. His apparatus is represented diagrammatically in Fig. 4-2. With a low gas pressure in the tube, an electrical discharge is maintained in the region D, the plate B being the cathode or negative terminal and A the anode or positive electrode. The evidence acquired by earlier experimenters, such as Plücker[1] and his students, and Hertz[2] and Perrin,[3] showed quite conclusively that in such a discharge at least part of the current is carried by negatively charged particles moving in approximately straight lines through the discharge tube. These negative particles are known as *cathode rays*. In Thomson's experiment, some of them, on reaching the anode, pass through a hole in it and on into the field-free region to the right. Here they are collimated by the second diaphragm A' and then pass between the condenser plates P and the coils of wire C and finally strike the fluorescent screen S. If the plates are at the same potential and there is no current flowing in the coils, the cathode rays excite a small luminous spot in the center of the screen. When a potential difference is applied to the plates, this spot is deflected in the direction which would be predicted if the cathode rays are a stream of negatively charged particles.

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[1] THOMSON, J. J., *Phil. Mag.*, **44**, 293 (1897); "Conduction of Electricity through Gases," 2d ed., p. 117, Cambridge University Press (1906).

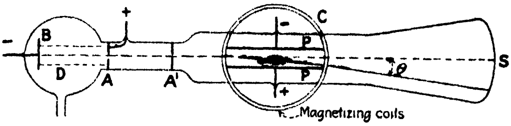

FIG. 4-2.—J. J. Thomson's apparatus to determine e/m of cathode rays.

Taking the direction of motion of the cathode rays (e) as the positive x-axis, the direction of the electric field as the positive z-axis, and the magnetic field as zero, we find, by integrating Eq. (4-3) over the length, L, of the plates that

$$\frac{dz}{dt} = -\frac{e}{m}E_z t = -\frac{e}{m}E_z\frac{L}{v_x}$$

where the minus sign is used because the charge on the particles is negative, and $t = L/v_x$ is the time for the particles to pass through the plates. The tangent of the angle of deflection θ of the fluorescent spot is given by the ratio of dz/dt to dx/dt, or

$$\tan\theta = -\frac{e}{m}E_z\frac{L}{v_x^2} \tag{4-4}$$

This result is not strictly accurate, since the electric field is not uniform over the whole region between the plates, but we may take it as sufficiently exact for our purpose. The velocity of the cathode rays, v_x, is still unknown. However, v_x may be found by sending a current through the coils of wire, so that a known magnetic field H_y, along the positive y-axis, extends over the region between the plates. This field is varied until the fluorescent spot is brought back to its undeflected position.

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[1] PLÜCKER, *Pogg. Ann.*, **107**, 77 (1859); **116**, 45 (1862).

[2] HERTZ, *Wied. Ann.*, **45**, 28 (1892).

[3] PERRIN, *Comptes Rendus*, **121**, 1130 (1895).

With such a combination of electric and magnetic fields, Eq. (4-3) becomes

$$m\frac{dv_z}{dt} = -eE_z - ev_xH_y$$

If the spot is undeflected, the acceleration in the z direction must be zero, so from this equation we have

$$v_x = -\frac{E_z}{H_y} \tag{4-5}$$

Combining this with Eq. (4-4), we find

$$\frac{e}{m} = -\frac{E_z}{LH_y^2}\tan\theta \quad \text{e.m.u. gram}^{-1} \tag{4-6}$$

where θ is the deflection before the magnetic field was applied. Thus e/m may be determined, but with the assumption that E_z and H_y are constant over the length L and zero elsewhere, which is certainly not correct. Thomson obtained $e/m = 7.7 \times 10^6$ e.m.u. per gram, and, about a year later, Lenard,[1] also working with cathode rays but with a slightly different experimental arrangement, obtained a value of 6.39×10^6 e.m.u. per gram. These are not in good agreement with the best modern determinations, but they are of the correct order of magnitude. Assuming that the charge carried by the particles comprising the cathode rays is the elementary unit charge 4.77×10^{-10} e.s.u. or

$$\frac{4.77 \times 10^{-10}}{3 \times 10^{10}} = 1.59 \times 10^{-20} \text{ e.m.u.}$$

the mass of the particles is found to be of the order of 10^{-27} gram.

4-4. e/m of Photoelectrons: Lenard's Method.—A still different method was employed by Lenard[2] to measure the ratio of charge to mass of the negative particles liberated from a metal plate under the influence of light. The apparatus is indicated in Fig. 4-3. Light enters the tube through the window W and liberates the negatively charged particles from the metal plate P. These are accelerated by an electric field E_x between P and the diaphragm S, through a hole in which the particles pass and reach the collector C_2, where their charge is measured with an electrometer. When a current is sent through the coils, the particles are deflected, and for a particular value of the magnetic field they reach the collector C_1, their charge being detected here also with an electrometer.

Let us assume that the region to the left of S is unaffected by the magnetic field and that to the right is free of any electric field. Taking the x-axis as positive in the direction of P to S, then in this region, Eq. (4-1) becomes

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[1] Lenard, *Wied. Ann.*, **64**, 279 (1898).

[2] Lenard, *Ann. Physik*, **2**, 359 (1900).

$$m\frac{dv_x}{dt} = -eE_x \tag{4-7}$$

or

$$m\frac{dv_x}{dx}\frac{dx}{dt} = mv_x\frac{dv_x}{dx} = -eE_x$$

or

$$\frac{m}{2}\frac{dv_x^2}{dx} = -eE_x$$

Integrating this, with the condition that the origin is taken at the hole in S, and P is distant L from S, along the negative x-axis, we have

$$\frac{m}{2}v_o^2 = -e\int_{-L}^{0} E_x dx = -eV \tag{4-8}$$

where v_o is written for the velocity of the particles at the origin, *i.e.*, as they pass through S, moving along the positive x-axis, and where V is the potential, in electromagnetic units, applied between P and S. This relation is useful in determining the energy, and hence the velocity, of any particle of known charge to mass ratio, provided the potential through which it has fallen is known.

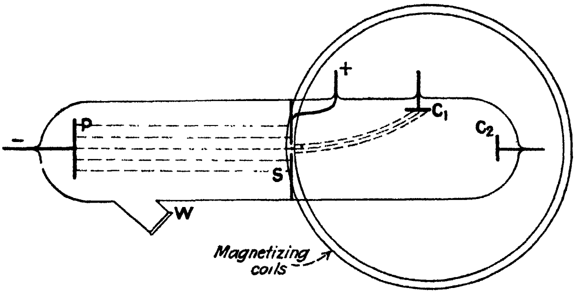

FIG. 4-3.—Lenard's apparatus to determine e/m of photoelectrons.

The velocity v_o is maintained after passing through the hole at S and the only subsequent force on the particle is that due to the magnetic field H_y. Since this force ev_oH_y is always perpendicular to the path, the trajectory becomes a circle of radius r. This may be shown from Eqs. (4-1) and (4-3). Equating the centripetal and centrifugal forces on the particle, we obtain

$$ev_oH_y = \frac{mv_o^2}{r} \tag{4-9}$$

Hence

$$r = \frac{m}{e}\frac{v_o}{H_y} \tag{4-10}$$

Eliminating v_c between Eqs. (4-8) and (4-10), we obtain

$$\frac{e}{m} = \frac{2V}{H_y^2 r^2} \text{ e.m.u. gram}^{-1} \tag{4-11}$$

If the x and z coordinates of the electrode C_1 are d_1 and d_2, respectively, we see geometrically from Fig. 4-4 that $r = (d_1^2 + d_2^2)/2d_2$. Hence from a knowledge of d_1 and d_2, and the values of V and H_y when the current to C_2 is a maximum, we may calculate e/m. This method, with certain refinements, is capable of great accuracy. Lenard obtained a value of about 1.2×10^7 e.m.u. per gram. Later, Alberti,[1] using a more refined apparatus, found e/m to be 1.765×10^7 e.m.u. per gram. Thus these light-liberated particles, or *photoelectrons*, are undoubtedly of the same nature as the cathode rays investigated by Thomson and others.

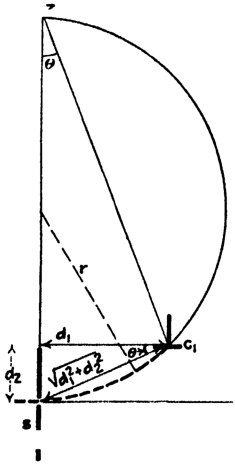

FIG. 4-4.—The geometrical relationships in Lenard's apparatus.

4-5. *e/m* of Thermoelectrons: Magnetron Method.—Another method of measuring e/m, applicable to the negatively charged particles, or thermoelectrons, emitted by a hot filament, is due to Hull.[2] If we have a very fine filament along the axis of a metal cylinder, in a uniform magnetic field which is also parallel to the axis, we can calculate the paths of electrons leaving the filament under the influence of the magnetic field and a radial electric field from Eqs. (4-1), (4-2), and (4-3).

From the discussion of the field between coaxial cylinders, in connection with the measurement of the electric units, in Chap. I, we know that the field between the filament and the cylinder is radial, and at a distance r from the axis is given by

$$-E_r = -\frac{V}{r \log_e \frac{b}{a}} \tag{4-12}$$

where b is the radius of the cylinder, and a that of the filament. The field is negative so that electrons are drawn away from the filament. There are no forces in the z direction (that of the axis) so the motion is entirely in the xy plane, if the electrons leave the filament normally. The paths of the electrons are approximately circular, and if H_z is the value of the magnetic field that just prevents the electrons from reaching the collecting cylinder, it may be shown that

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[1] ALBERTI, *Ann. Physik*, **39**, 1133 (1912).

[2] HULL, *Phys. Rev.*, **18**, 31 (1921).

$$\frac{e}{m} = \frac{8V}{b^2H_z^2}\frac{1}{\left(1 - \frac{a^2}{b^2}\right)^2} \text{ e.m.u. gram}^{-1} \tag{4-13}$$

A difficulty with this method is that the value of the magnetic field, at which the current ceases to flow to the cylinder, is not sharply defined. Nevertheless, the value of e/m obtained is in excellent agreement with those found for cathode rays and photoelectrons. Hence the presumption is very strong that all these particles are of the same nature.

Derivation of Eq. (4-13). The Eqs. (4-1) and (4-2) become:

$$m\frac{dv_x}{dt} = eE_x - ev_yH_z \tag{4-14}$$

$$m\frac{dv_y}{dt} = eE_y + ev_xH_z \tag{4-15}$$

As there is no component of E perpendicular to the radius vector, it is more convenient to transform x and y into polar coordinates, r and θ. The velocity along r is $v_r = dr/dt$, and the velocity perpendicular to r is $v_\theta = r\,d\theta/dt$. Then

$$v_x = v_r \cos\theta - v_\theta \sin\theta$$

and

$$v_y = v_r \sin\theta + v_\theta \cos\theta$$

Also

$$E_x = E_r \cos\theta$$

and

$$E_y = E_r \sin\theta$$

If we substitute these in Eqs. (4-14) and (4-15), and then further multiply Eq. (4-14) by $\sin\theta$ and Eq. (4-15) by $\cos\theta$ and then subtract, we obtain

$$m\left(v_r\frac{d\theta}{dt} + \frac{dv_\theta}{dt}\right) = eH_zv_r$$

or

$$2\frac{dr}{dt}\frac{d\theta}{dt} + r\frac{d^2\theta}{dt^2} = \frac{eH_z}{m}\frac{dr}{dt}$$

or

$$\frac{1}{r}\frac{d}{dt}\left(r^2\frac{d\theta}{dt}\right) = \frac{eH_z}{m}\frac{dr}{dt} \tag{4-16}$$

This equation may be integrated by separating the variables

$$\frac{d}{dt}\left(r^2\frac{d\theta}{dt}\right) = \frac{eH_z}{2m}\frac{dr^2}{dt}$$

$$\left[r^2\frac{d\theta}{dt}\right]_a^r = \frac{eH_z}{2m}\left[r^2\right]_a^r$$

If we assume that the electrons leave the filament normally to its surface, then $d\theta/dt = 0$ at $r = a$, and we obtain

$$\frac{d\theta}{dt} = \frac{eH_z}{2m}\left(1 - \frac{a^2}{r^2}\right) \tag{4-17}$$

If we multiply Eq. (4-14) by $\cos\theta$, and Eq. (4-15) by $\sin\theta$, after making the substitutions for polar coordinates, and then add the two equations so obtained, we get

$$m\left(\frac{dv_r}{dt} - v_\theta\frac{d\theta}{dt}\right) = eE_r - eH_zv_\theta$$

or

$$\frac{d^2r}{dt^2} - r\left(\frac{d\theta}{dt}\right)^2 = \frac{e}{m}E_r - \frac{eH_z}{m}r\frac{d\theta}{dt} \tag{4-18}$$

We substitute for $d\theta/dt$ from Eq. (4-17) and find

$$\frac{d^2r}{dt^2} = \frac{e}{m}E_r - r\left(\frac{eH_z}{2m}\right)^2\left(1 - \frac{a^4}{r^4}\right) \tag{4-19}$$

Remembering that

$$\frac{d^2r}{dt^2} = \frac{d}{dt}\frac{dr}{dt} = \frac{dr}{dt}\frac{d}{dr}\frac{dr}{dt} = \frac{1}{2}\frac{d}{dr}\left(\frac{dr}{dt}\right)^2$$

we may integrate Eq. (4-19) between the limits a and r, assuming that the electrons leave the filament with negligible velocity (*i.e.*, $dr/dt = 0$ at $r = a$),

$$\left(\frac{dr}{dt}\right)^2 = 2\frac{e}{m}V - \left(\frac{eH_z}{2m}\right)^2 r^2\left(1 - \frac{a^2}{r^2}\right)^2 \tag{4-20}$$

Here V has been written for $\int_a^r E_r\,dr$. We could integrate Eqs. (4-17) and (4-20), eliminate t and so obtain the equation of the path of a particle, which would be approximately a circle, but it is sufficient for our purposes to obtain an expression for the maximum distance from the filament that is attained by an electron. This is found by setting $dr/dt = 0$ in Eq. (4-20). If this maximum value of r is equal to b, the radius of the cylinder, we obtain Eq. (4-13). If the charge due to the electrons in the region between the filament and cylinder is taken into account, the resulting equation for e/m is the same. If the small velocities of the electrons on leaving the filament are included, the calculations are more complicated, and a small correction term is introduced into the expression for e/m.

4-6. *e/m* of β Rays.—It has been found, as will be further discussed in connection with radioactivity, that certain substances spontaneously emit negatively charged particles. Their ratio of charge to mass was measured by Kaufmann,[1] and later and more accurately by Bestelmeyer[2] and by Bucherer.[3] The method employed in this later work is shown diagrammatically in Fig. 4-5. The negative particles leaving the source at S pass through the narrow region between the condenser plates P and strike the photographic plate at R. The entire apparatus is evacuated and placed in a strong magnetic field, perpendicular to the direction of motion and to the electric field between the plates. Under these circumstances, only those particles which are moving in the x direction from S to R with the velocity $v_x = -E_z/H_y$ [see Eq. (4-5)] are not deflected and hence do not strike one of the condenser plates and so leave the beam. When this stream of particles with uniform velocity v_x leaves the region of the electric field, it is then affected only by the magnetic field, and it is

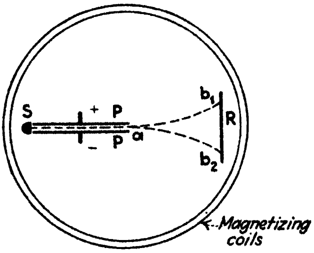

FIG. 4-5.—Bucherer's apparatus to determine e/m of β rays.

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[1] KAUFMANN, *Physik. Zeits.*, **4**, 54 (1902); *Ann. Physik*, **19**, 487 (1906).

[2] BESTELMEYER, *Ann. Physik*, **22**, 429 (1907).

[3] BUCHERER, *Ann. Physik*, **28**, 513 (1909).

bent into a circle of radius $r = v_x m/eH_y$, as follows from Eq. (4-10), and traverses the path ab_1. If the electric and magnetic fields are reversed, the deflection is in the other direction and the path ab_2 is described. Suppose the distance on the photographic plate between the spots b_1 and b_2 is $2d_2$, and the distance from the ends of the condenser plates to R is d_1, we then have $r = \dfrac{d_1^2 + d_2^2}{2d_2}$ as in Fig. 4-4. Eliminating v_x between the two previous equations and then substituting for r, we find

$$\frac{e}{m} = -\frac{2d_2}{d_1^2 + d_2^2}\frac{E_z}{H_y^2} \text{ e.m.u. gram}^{-1} \tag{4-21}$$

and

$$v_x = -\frac{E_z}{H_y} \tag{4-22}$$

Hence v_x and e/m are both found from a knowledge of E_z, H_y, d_1 and d_2. Bucherer found that the values of e/m, obtained for β rays of different velocities from various radioactive sources, were not the same. The velocities measured were very large indeed, ranging from 9.5×10^9 to 2.06×10^{10} cm. per second. The values of e/m lay between 1.66×10^7 and 1.28×10^7 e.m.u. per gram.

There is no reason to suppose that the charge should not be constant, but, on the other hand, the theory of relativity predicts that mass should vary with velocity. As we have seen in Chap. I, Eq. (1-26), the relationship is

$$m = \frac{m_0}{\sqrt{1 - \dfrac{v^2}{c^2}}}$$

where m is the mass as measured by an observer with respect to whom the body has a velocity v, and m_0 is the rest mass. If we apply this equation to reduce the values of e/m obtained for β rays to the values of e/m_0, we find (Bucherer) the results given in the following table.

v/c	e/m	e/m_0
0.3173	1.661×10^7	1.752×10^7
0.3787	1.630	1.761
0.4281	1.590	1.760
0.5154	1.511	1.763
0.6870	1.283	1.767

This brings very good agreement between otherwise discordant results, and it is considered to be one of the best experimental verifications of the predicted variation of mass with velocity. It would be even more convincing if a larger quantity of evidence on the value of e/m for

β rays were obtained with more advanced vacuum technique and other experimental methods.

4-7. *e/m* of Thermoelectrons: Busch Method.—The most accurate evaluation of e/m for thermoelectrons involving magnetic deflection has been performed by Wolf,[1] using a method due to Busch.[2] The general arrangement is indicated in Fig. 4-6. Electrons leave the filament F and are accelerated to the diaphragm D_1 by an electric field. The velocity of the electrons on passing through the hole in D_1 is given by the energy relation of Eq. (4-8). The electrons then spread out into a cone and strike the diaphragm D_2, in which is cut a circular slit, the center of the circle lying along the axis of the cone of electrons, which we may take as the x-axis. Only those electrons whose paths lie in the conical shell of semiapex angle α pass beyond D_2. A uniform magnetic field H_x is maintained along the x-axis, between D_1 and D_3, and this region is free of any electric field. A fluorescent screen is located at D_3. The velocity components perpendicular and parallel to the magnetic field are $v \sin \alpha$ and $v \cos \alpha$ respectively, where v is the total velocity as given by Eq. (4-8). The projected motion in the yz plane is therefore a circle of radius given by Eq. (4-10)

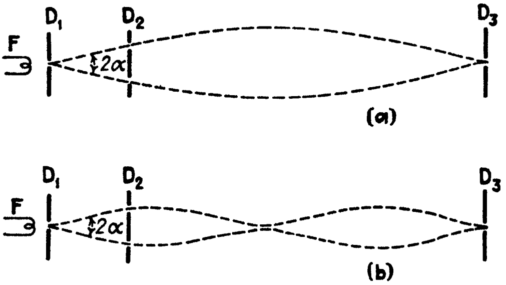

Fig. 4-6.—Busch's apparatus to determine e/m of thermoelectrons. In (*a*) electrons are shown traveling from D_1 to D_3 in one turn of their helical path. In (*b*) they make two turns while traversing the same distance.

$$r = \frac{mv}{e} \frac{\sin \alpha}{H_x}$$

The path in space of an electron is therefore a helix whose axis is parallel to H_x. The time for a complete revolution of one electron is

$$\tau = \frac{2\pi r}{v \sin \alpha} = 2\pi \frac{m}{eH_x}.$$

and hence each electron, having started from the x-axis, returns to it at multiples of this interval. If, during a time $n\tau$, where n is an integer, the electrons have traveled the distance L from D_1 to D_3, along the x-axis, they will come to a focus at the center of the fluorescent screen D_3. Therefore,

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[1] Wolf, *Ann. Physik*, **83**, 849 (1927).

[2] Busch, *Physik. Zeits.*, **23**, 438 (1922).

$$L = v_x n\tau = 2\pi \frac{m}{eH_x} nv \cos \alpha$$

and since $\frac{m}{2}v^2 = eV$, we have,

$$\frac{e}{m} = \frac{8\pi^2 V}{L^2 H_x^2} n^2 \cos^2 \alpha \quad \text{e.m.u. gram}^{-1} \tag{4-23}$$

Therefore, if, say, the magnetic field is held constant and the potential V is increased, electrons will be focused on D_3 at potentials that are inversely as the square of a decreasing series of integers; for $n = 1$, the electrons travel the length of the tube in a single turn of their helical path. From the known dimensions of the apparatus, e/m may thus be found. Using such a method and applying many corrections that we shall not discuss, Wolf obtained the value

$$(1.7679 \pm 0.0018) \times 10^7 \text{ e.m.u. gram}^{-1},$$

in international units for the quantities involved in the measurement. This, when corrected[1] to absolute units, is

$$\frac{e}{m_0} = (1.7689 \pm 0.0018) \times 10^7 \text{ e.m.u. gram}^{-1}$$

Method of Dunnington.—A very interesting and novel means of determining e/m has been described by Dunnington.[2] A high-frequency oscillator is coupled to a filament and near-by grid, so that an alternating e.m.f. is applied between the two. During those half cycles in which the grid is positive, groups of electrons are accelerated with velocities ranging from zero to a maximum corresponding to the peak voltage. A magnetic field bends the paths of the electrons into circles of varying radii, and a series of slits permits those of a particular radius of curvature to enter a collecting chamber connected to an electrometer, the total path for these electrons being a little less than a complete circle. Just in front of the collector are two grids, also coupled to the oscillator, in such a manner that if an electron makes the journey in exactly one cycle of the oscillation it is subjected to a retarding force just equal to the accelerating force that it experienced before, and hence it does not enter the collector. For a given frequency and potential applied to the oscillator plate, there is therefore a critical magnetic field for which no electron current is recorded.

Equating the centripetal and centrifugal forces on the electron, we obtain, as in Eq. (4-10),

$$Hr = \frac{mv}{e}$$

The path is a circular arc of θ radians and radius r, so that the length is $L = r\theta$ and hence the velocity is

$$v = \frac{L}{T} = r\theta\nu$$

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[1] BIRGE, *Phys. Rev. Suppl.* (*Rev. Mod. Phys.*), **1**, 1 (1929).

[2] DUNNINGTON, *Phys. Rev.*, **42**, 734 (1932); **43**, 404 (1933).

T being the period and ν the frequency of the oscillator. Eliminating v between these equations we find

$$\frac{e}{m} = \frac{\theta\nu}{H} \text{ e.m.u. gram}^{-1}$$

It should be noted that in distinction to the other deflection methods of measuring e/m, neither the velocity nor the radius of curvature appears in the final equation. The angle θ is found from the geometry of the apparatus, with a goniometer or otherwise; the magnetic field H is calculated from the dimensions of the coils of wire and the current flowing in them (the earth's field having been balanced out); the frequency ν is determined by heterodyne comparison of the harmonics of the carrier wave of a reliable broadcasting station or of a local crystal-controlled oscillator of known frequency. To find e/m_0, a small correction for the relativity change in mass with velocity must be made. For this purpose, the velocity is obtained by the use of Eq. (4-10), with a rough measure of r and the value of e/m already determined.

This method appears to be considerably more sensitive and capable of higher precision than any other yet devised and, in preliminary form, has given results in excellent agreement with the best previous values.

4-8. Experimental Measurement of e/m: Magnetic Deflection Methods.—With moderate glass-blowing facilities, it is very easy to construct a tube suitable for the application of one of the above methods of measuring e/m. A convenient simple design for any particular method will readily suggest itself from the preceding discussion and references. But inasmuch as there are several more or less suitable tubes that may be obtained commercially, the following brief discussion will be confined to these.

Magnetron.—The commercial magnetron consists of a highly evacuated tube containing a straight filament and a coaxial cylindrical electrode. It is placed in the center of a coil of wire which is suitably designed so that the magnetic field is parallel to the filament and uniform over the region of the cylindrical electrode. The system is then oriented so that the magnetic field is parallel to that of the earth. If the latter is known, the effective field may be found by adding the earth's field to that calculated from the current in the coil. The potential difference between the filament and cylinder may be measured with a voltmeter, and the radii of the filament and cylinder found by means of a cathetometer. The value of e/m is found from Eq. (4-13). If the strength of the earth's field is not known, the current through the coil may be reversed, so that the two fields are opposed. The difference between the fields due to the coil, when electrons just fail to reach the cylinder, for the two directions of current, is seen to be equal to twice the earth's field. Hence this latter field may be determined and e/m found as before. Further experimental points and refinements in the calculations are given in the paper by Hull to which reference has already been made.[1]

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[1] HULL, *Phys. Rev.*, **18**, 31 (1921).

Radio Tube.—A still simpler but slightly less accurate arrangement is to use an ordinary type of cylindrically symmetric radio tube. As these tubes are generally not highly uniform, it is necessary to choose one in which the filament is as nearly as possible along the axis of the cylindrical plate. This may best be judged by the sharpness of the plate-current cut-off, as the magnetic field is increased. The field may be produced conveniently by a long single-layer solenoid and may be calculated from the relation

$$H = \frac{4\pi nI}{10} \text{ e.m.u.}$$

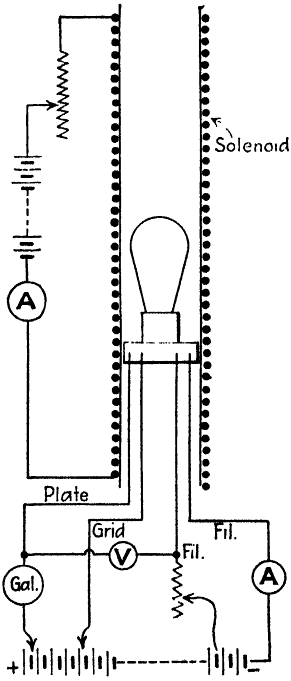

FIG. 4-7.—The magnetron method, using a radio tube with cylindrical symmetry, for determining e/m of thermoelectrons.

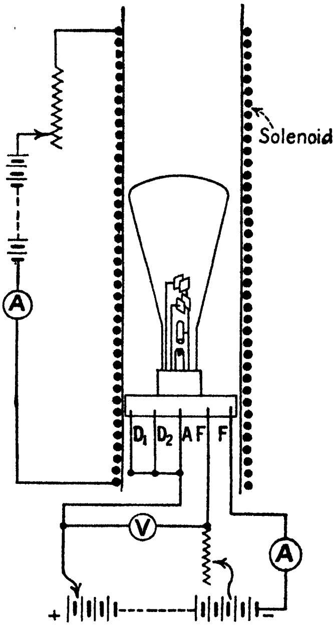

FIG. 4-8.—A Braun cathode-ray tube used in the Busch method of determining e/m of thermoelectrons.

where n is the number of turns of wire per centimeter length of solenoid, and I is the current in amperes. An error of less than 1 per cent is made in calculating the field from this equation, if the length of the solenoid is more than seven times its diameter. The tube is mounted in such a solenoid as shown in Fig. 4-7, and the procedure is the same as for a magnetron. The grid of the tube should be sufficiently positive with respect to the filament so that a good emission from the filament is obtained. It can be shown that the magnitude of this potential does not affect the value of e/m obtained. Measurement of the diameters of the electrodes may be made with a cathetometer if the tube is properly illuminated. For purposes of observation the "getter" may be removed from an area of the glass bulb by gentle local heating with a gas flame.

Cathode-ray Oscillograph Tube.—A Braun tube may be adapted to give reasonably accurate values of e/m by either the Busch or the Lenard method.

For the Busch method, a solenoid may be wound large enough to contain the cathode-ray tube, as shown in Fig. 4-8. The deflecting plates are all connected to the anode. The filament current and applied electric field between the filament and the anode are adjusted, so that the spot on the fluorescent screen at the end of the tube is out of focus. Then the current in the solenoid is adjusted to give the best focus. The axis of the solenoid should lie in the earth's field, so that the effective field may be calculated. For approximate results, the earth's field may be neglected. The potential between filament and anode is measured with a voltmeter, L may be found with a cathetometer, and the angle α may be taken as zero, to a first approximation. The exact condition of focus is uncertain, as there is no well-defined value of α. The value of e/m is found from Eq. (4-23).

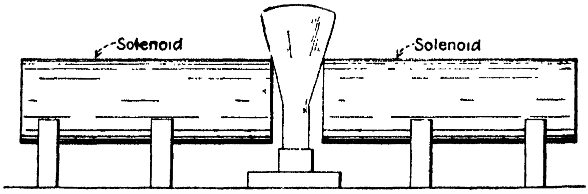

FIG. 4-9.—A Braun cathode-ray tube used in a method approximating that of Lenard, to determine e/m of electrons.

An oscillograph tube may be used in several ways analogous to that of Lenard to obtain e/m. Two solenoids a few inches in diameter may be mounted on either side of the tube, as shown in Fig. 4-9. The deflecting plates are connected to the anode and the fluorescent spot is focused by adjusting the filament current. The deflection of the spot, for a given current in the coils, is measured with a paper scale placed against the end of the tube. The current in the coils is then reversed and the deflection in the opposite direction is recorded. This is done with the coils as close to the tube as possible. A series of such measurements is made for a succession of distances of the coils from the tube, and from these a graph may be drawn, which on extrapolation gives the deflection to be expected if the solenoid were continuous through the tube. This extrapolation is chiefly responsible for the inaccuracy of the method. From this deflection, the potential V, the calculated field H, and the necessary geometrical measurements, we may calculate e/m from Eq. (4-11).

An accurate and very simple way to use a cathode-ray tube for the determination of e/m is to employ the earth's field for the deflecting force. This field must be measured accurately with a magnetometer and dip circle at the place where the experiment is to be performed. The cathode-ray tube is mounted in a framework so that it may be rotated about a horizontal axis, as shown in Fig. 4-10. The apparatus is oriented so that the axis of rotation is perpendicular to the earth's field. The deflecting plates are connected to the anode, and the spot is focused by adjusting the filament current. The tube is then rotated about the horizontal axis until the maximum deflection of the spot to one side or the other is obtained. The axis of symmetry of the tube is then perpendicular to the earth's field. If the tube is then rotated through 180° about the horizontal axis, the maximum deflection in the other direction will be observed. The distance between the extreme positions of the spot, which is of the order of several centimeters, may be measured with a paper scale across the fluorescent screen. One half of this distance is the deflection that would be produced by the earth's field acting on electrons moving perpendicularly to it with a velocity given by $mv^2/2 = eV$, where V is the potential, in electromagnetic units, applied between the filament and the anode. Hence from this deflection, the necessary dimensions, which may be measured with a cathetometer, the value of the total component of the earth's field, and the potential V, we may calculate e/m by Eq. (4-11). Results may be obtained by this method agreeing with the accepted value to within about 1 per cent.

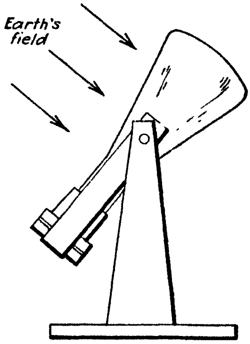

FIG. 4-10.—A Braun cathode-ray tube used to determine e/m of electrons with the aid of the earth's magnetic field.

4-9. Electrostatic Methods of Determining e/m. *Space-charge Method.*—This depends on the potential-current relation existing for the flow of electrons from a heated filament to a coaxial cylindrical electrode, when the current is limited not by the total number of electrons emitted by the filament but by the *space charge* of the electrons present in the region between the filament and the collector. This method was used by Dushman,[1] and will be discussed in connection with thermionic emission in Chap. VI.

Velocity-filter Method.—This method, due to Des Coudres[2] and first used by Wiechert,[3] has been rendered a method of great precision by

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[1] DUSHMAN, *Phys. Rev.*, **4**, 121 (1914).

[2] DES COUDRES, *Verh. Deut. Physik. Ges.*, **14**, 157 (1897).

[3] WIECHERT, *Ann. Physik*, **69**, 739 (1899).

Perry and Chaffee[1] and by Kirchner.[2] The principle is very simple and is indicated in Fig. 4-11. Electrons leaving the filament F are accelerated by a potential V between the filament and the diaphragm D_1. Some of the electrons pass through a hole in D_1 and, after traveling between the condenser plates P_1, reach the diaphragm D_2. If there is no field between the plates P_1, they go through a hole in the center of D_2, but if a field exists while the electrons are passing between the plates, they are deflected to one side or the other and miss the hole in D_2. Beyond D_2 is another pair of condenser plates P_2, between which the electrons pass on their way to the fluorescent screen S. If there is no field at P_2, the electrons strike the center of the screen, but they are displaced to one side if a potential exists across P_2 as they go through.

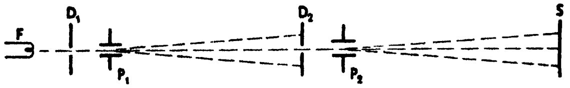

Fig. 4-11.—The Wiechert method of determining e/m of electrons.

Hence if an alternating potential is applied across P_1, the beam of electrons is spread out as indicated by the dotted lines in Fig. 4-11. Suppose the sine curve in Fig. 4-12 represents this potential difference as a function of the time; then only those electrons which pass P_1, approximately at the times A, B, C, D, etc., will go through the hole in D_2. If the same alternating potential is applied to P_2, the electrons passing between these plates will be subject to the field between them that exists at a time t after one of the points A, B, C, D, etc., where t is the distance L between P_1 and P_2 divided by the velocity of the electrons. If either this velocity or the frequency of the alternating field is adjusted so that the fluorescent spot occupies the same central position on the screen that it

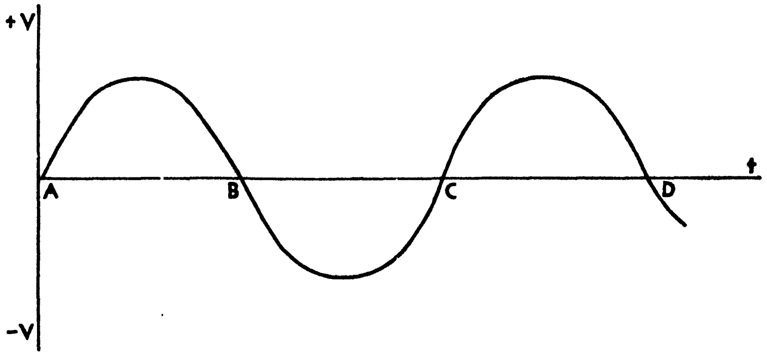

Fig. 4-12.—The alternating potential applied to the deflecting plates of Fig. 4-11.

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[1] Perry and Chaffee, *Phys. Rev.*, **36**, 904 (1930).

[2] Kirchner, *Ann. Physik*, **8**, 975 (1931).

does when no field is applied at all, then the time of passage is that given by a distance along the time axis such as that between AB, AC, or AD; *i.e.*, $t = n\tau/2$, where τ is the period of the alternating potential and n is an integer. Therefore,

$$\frac{n\tau}{2} = \frac{L}{v} \quad \text{and} \quad \frac{mv^2}{2} = eV$$

so that

$$\frac{e}{m} = \frac{2L^2}{n^2\tau^2V} \tag{4-24}$$

where V is in electromagnetic units. The quantities L, τ, and V may be measured with great accuracy; if the position of the spot on the fluorescent screen is well defined, so that the condition for the application of Eq. (4-24) can be accurately ascertained, the value of e/m can be determined with great precision. To find e/m_0 by this method with an accuracy of about 0.1 per cent, it is necessary to correct for the finite length of the condenser plates, the difference between the absolute and the international units, and the relativity dependence of mass on velocity. The resolving power of the apparatus and the necessary corrections are discussed by Kirchner. The value of e/m_0 found by him is

$$\frac{e}{m_0} = (1.7598 \pm 0.0025) \times 10^7 \text{ e.m.u. gram}^{-1}$$

The value found by Perry and Chaffee is of the same order of accuracy and is in excellent agreement with this result.

The discrepancy between this value and that found by Wolf with magnetic deflection, $(1.7689 \pm 0.0018) \times 10^7$, is larger than can be accounted for by the known experimental errors. The best spectroscopic determinations of this quantity are those of Houston,[1] obtained from the line spectra of hydrogen and helium, and of Babcock,[2] found from measurements of the Zeeman splitting of spectral lines of zinc and cadmium. They obtained values of $(1.7608 \pm 0.0008) \times 10^7$ and $(1.7606 \pm 0.0012) \times 10^7$, respectively. Recent work by Campbell and Houston[3] by the Zeeman effect method gives the value $(1.7579 \pm 0.0025) \times 10^7$. In accordance with our present theories, these represent the ratio of the charge to mass of electrons bound in an atomic system. In view of the excellent agreement of these spectroscopic results with those of Kirchner, it is probable that there is some undiscovered source of error in the measurements of Wolf, rather than that a difference exists between the value of this ratio for free electrons and for those bound in an atom, as had been suggested before the publication of Kirchner's work. The equations of motion for the center of gravity of an electron on quantum-mechanical principles, under the conditions here considered, are the same as those which have been deduced on the basis of classical electrical theory; hence there is no possibility of explaining the discrepancy on the grounds of a failure of the classical theory.

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[1] HOUSTON, *Phys. Rev.*, **30**, 608 (1927).

[2] BABCOCK, *Astrophys. J.*, **69**, 43 (1929).

[3] CAMPBELL and HOUSTON, *Phys. Rev.*, **39**, 601 (1932).

The general conclusion which may be drawn from the work on e/m to date is that free electrons obtained from all known sources as well as those bound in atomic systems are identical in nature and have the ratio of their charge to their mass given by[1]

$$\frac{e}{m_0} = (1.761 \pm 0.001) \times 10^7 \text{ e.m.u. gram}^{-1}$$

Further properties of electrons, such as the emission of radiation by them, their magnetic moment, and their behavior in a manner which may best be described by the conception of them as wave trains, will be discussed in subsequent chapters.

4-10. Experimental Measurement of e/m: Velocity-filter Method.—The construction of a tube which has been used successfully to measure e/m will be described briefly. Variations in details of structure and operation will readily suggest themselves. The apparatus is essentially similar to that of Kirchner; its main features are shown in Fig. 4-13. The tube itself is a brass pipe 5 or 6 cm. in diameter and 115 cm. long. The two pairs of plates, P_1 and P_2, are supported on rods let through the walls of the tube in bakelite plugs, the centers of the holes for these plugs being 50 cm. apart. The plates are 1 cm. square and separated by about 0.5 cm. The diaphragms in front of these plates are brass disks which just fit the inside of the tube and are held in place by pins. The holes in the center of the diaphragms are 0.2 cm. in diameter. The filament side of the diaphragm in front of P_2 is painted with fluorescent material which may be observed through the glass window W waxed over a hole in the brass tube. This greatly facilitates the adjustment of the electron beam. On the end of the tube beyond P_2 is waxed a piece of plate glass S, on the inside of which fluorescent material has also been painted. These fluorescent screens may be easily prepared by sifting a mixture of luminous zinc sulphide and calcium tungstate upon a thin, freshly applied coat of varnish. The material of a fluorescent screen such as that from an old Braun tube may be scraped off and used very satisfactorily.

The direction of the earth's magnetic field is ascertained with a dip circle and a compass, and the tube is mounted with its axis as nearly as possible in the field. One of the vacuum-pump connections is made from the region surrounding the filament, as it is from here that most of the adsorbed gas is liberated during operation of the tube. The pumps are run continuously and a pressure of about 10^{-4} or 10^{-5} mm. Hg is maintained.

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[1] BIRGE, *Phys. Rev. Suppl.* (*Rev. Mod. Phys.*), **1**, 1 (1929).

Several arrangements of the cathode are possible and will give results quite as good as the one described here. The entire cathode unit is mounted on a three-stem tungsten-in-Pyrex base, which is waxed into the end of the tube. The joint may be cooled with a wet cloth and a jet of air, if it threatens to soften because of the heat from the filament. The latter is either a small tight spiral of 5-mil tungsten wire or a short platinum strip notched at the center and painted with barium and strontium oxides in varnish. It is necessary to have an emission of only 2 or 3 milliamp. Attached to the filament supports is a cylindrical metal shield about 4 cm. long and 1.5 cm. in diameter; this tends to collimate the electron beam along the axis of the tube. The third stem supports a plate D, with a 0.5-cm. hole in its center, in front of this shield. The electrons are thus subjected to two accelerating fields, the first between the filament and the plate D, the second between D and the diaphragm D_1, which is in electrical contact with the body of the tube. The latter is grounded, for safety, and the fields are adjusted by the contacts b_1 and b_2 on the potentiometer shunted across the source of potential. The purpose of the two fields is to obtain the focusing effect on the electron beam which adjustment of the two fields permits. The total potential through which the electrons fall is read from a high-resistance voltmeter.

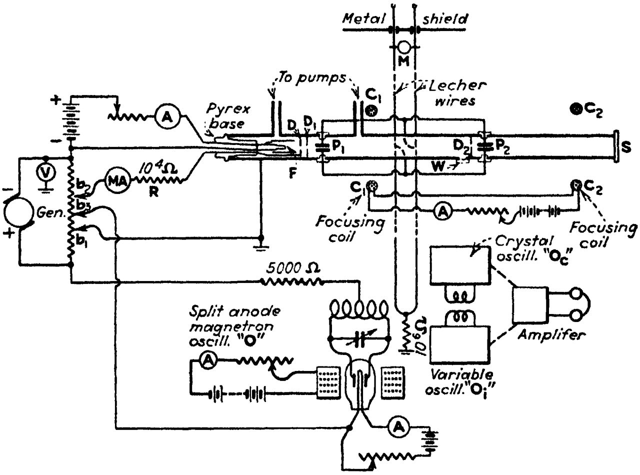

FIG. 4-13.—The Wiechert type of velocity filter for measuring e/m of electrons.

The simplest procedure is to vary the fields until the fluorescent screen, viewed through the window W, is brightest. If the beam at this point is so diffuse that the intensity at the screen S is insufficient, the focusing coils C_1 and C_2 may be added, the first to concentrate the electron beam (after the manner of the Busch method of measuring e/m) more or less on the hole in D_2, and the second again to bring the beam together at the screen S. The focus at D_2 must be only approximate, however, or there will be no motion of the beam produced when an alternating field is applied to the deflecting plates. The plane of the coils may also be adjusted to compensate for any lack of alignment with the earth's field. Coils of a few hundred turns will give as large a field as is necessary.

The potential applied to the tube may be obtained from a 2,000-volt direct-current generator. The protective resistance R, of about 10,000 ohms, should be inserted in the lead to the plate D to prevent arcing when the filament emits gas. The resolving power of the apparatus as a velocity filter, *i.e.*, the smallest per cent change in the velocity which may be detected, varies as the inverse $\frac{3}{2}$ power of the potential V, so from this standpoint low voltages are desirable. It is difficult to obtain a bright fluorescent spot below 1,000 volts, so the range between 1,000 and 2,000 volts is the most convenient in which to work. This potential may be obtained from any other source capable of supplying the necessary current with a voltage fluctuation small enough to give acceptable accuracy.

The alternating electric fields are applied to the deflecting plates by means of the Lecher wire system shown in Fig. 4-13. The mid-points of the Lecher wires are connected to the centers of wires which symmetrically join pairs of the plates P_1 and P_2. The junctions with the Lecher wires are made with clips so that their position may be changed when alterations are made in the Lecher wires for tuning purposes. Various types of oscillators may be used to excite the system. The diagram indicates the use of a split anode magnetron, O. The inductance is a helix of copper tubing of 10 turns about 8 cm. in diameter. A 50-$\mu\mu$f. variable condenser, operated by a long glass handle to reduce body capacity, provides fine adjustment of the tuning. An ordinary Hartley circuit employing a power oscillator or amplifying radio tube, with a plate potential of 300 or 400 volts, is also satisfactory. The resolving power of the apparatus is theoretically proportional to the field between the deflecting plates.

The measurement of the frequency is performed by means of heterodyne beats with a crystal-controlled oscillator of several hundred kilocycles per second, O_c, through the intermediate frequency oscillator O_i. The amplifier A is placed in the circuit of the oscillator whose harmonic is to be detected. The oscillator O_i is adjusted so that its fundamental frequency makes a "zero-beat" note with a high harmonic of the crystal, say, the fifteenth. Then the amplifier is transferred from the crystal to the intermediate oscillator, and the driver O is adjusted so that its fundamental, of approximately the desired frequency, gives a zero-beat note with a harmonic of O_i. Which harmonics are being used, is found from a previous rough calibration of the oscillators with a wave meter. Finally, the Lecher wires are tuned by sliding the short-circuiting thermo-milliammeter M along the far end of the wires. The meter is backed up by a large metal shield, through insulated holes in which the Lecher wires pass; this is to reduce the detuning effect of the ends of the wires beyond the meter. Resonance is indicated very sharply by the meter reading. The length of each of the Lecher wires, in resonance with a frequency of about 25,000 kilocycles per second (about 14 meters), is about 1 meter less than the half wave length, due to the capacity of the deflector plates and the inductance of the single half loop and meter at the ends of the wires. When the system is oscillating in this manner, current loops exist at the ends, *i.e.*, at the meter and the end near the driver, while there is a voltage loop at the plates P_1 and P_2.[1]

After preliminary adjustments have been made, the patterns observed on the screen S are noted for a range of values of the accelerating potential obtained by varying the contact b_1. The patterns consist of two spots except over a range of about 50 volts, where they blend into one, occurring at each critical potential defined by successive integral values of n in Eq. (4-24). For a path length between plates of 50 cm. and using 25,000 kilocycles, the highest critical voltage of the electrons, corresponding to $n = 1$, is about 1,800 volts. These two spots are due to two sets of electrons; those passing P_1 at such points as A, C, etc., in Fig. 4-12, and those passing P_1 at B, D, etc. If their velocity is slightly greater or less than a critical value, these two groups, which left P_1 half a cycle apart, are acted on by fields in opposite directions when they reach P_2. The potential corresponding to the mid-point of the voltage range in which but one spot is visible may be taken as the correct value for use in Eq. (4-24). At 1,800 volts, the velocity of the electrons is such that the relativity mass correction is a little less than $\frac{1}{2}$ per cent, but, as this is barely outside the limits of accuracy of the suggested procedure, the correction is of little significance.

4-11. The Ratio *e/M* of Positive Ions.—In Chap. III we saw that the number of molecules in a gram-molecule, N, of any substance, could be determined from measurements on the Brownian motion, if the electronic charge e and the gas constant R are known. R may be found from a measurement of the pressure and volume of a gram-molecule of a gas at a known temperature by the relation $R = pV/T$, the gram-molecule being determined by weighing, since this quantity is the molecular weight expressed in grams. N may also be found from the measured mass of some substance that is deposited in electrolysis by a known quantity of electricity, provided that the atomic weight and valence of the element, as well as the electronic charge, are known.

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[1] For the construction of oscillators and Lecher wire systems, and for the measurement of frequency by means of beats, the reader is referred to a text on radio-frequency measurements, such as: Brown, "Radio Frequency Electrical Measurements," McGraw-Hill (1931). Practical suggestions for the operation of oscillators may be found in "The Radio Amateur's Handbook," The American Radio Relay League, Hartford, Conn. (1932).

Thus, from a knowledge of Avogadro's number N (6.06×10^{23} per gram-molecule) and the atomic weight, the average mass of any atom may be found. The atomic weight of an oxygen atom is exactly 16 by definition, so there are 6.06×10^{23} molecules in a quantity of oxygen that has a mass of 32.0000 grams, since the oxygen molecule is diatomic; therefore, the molecule has a mass of $32/(6.06 \times 10^{23})$ or 5.28×10^{-23} gram, and the atomic mass is one-half of this. Similarly, the mass of any other atom may be found by dividing its experimentally determined atomic weight by Avogadro's number, on the basis of the arbitrary value of 16 for oxygen.

We note that this method of ascertaining the mass of any atom really determines only the average mass of a large number of chemically identical atoms. Atomic weights are found, in principle, by weighing quantities of materials that combine in known proportions with oxygen. It has been found that the chemical properties, and therefore the combining abilities of atoms, do not depend on the mass of the nucleus, but only on the number of electrons external to it, the mass of these electrons being negligible. Hence if several varieties of an element exist, with different masses in the nuclei but with similar external electrons, their chemical properties will be identical. If we divide the mass of a gram-molecule of such a substance by Avogadro's number, we obtain merely the average mass of its molecules.

The existence of these so-called *isotopes*, or varieties of elements having similar chemical properties but different masses, has been proved experimentally by methods which we shall discuss presently. Their occurrence accounts, to a first approximation, for the fact that many atomic weights are not integers, contrary to what would be expected on Prout's hypothesis. These atomic weights are now known to be the average of the atomic weights of two or more isotopes.

The more important methods that do not depend on a knowledge of the atomic weight for determining atomic masses are based on the measurement of the ratio of the charge on an ion to its mass. In some convenient way, generally by electron bombardment, an electron is removed from the atomic system whose mass is to be determined, for a time long enough for the ratio of e/M to be measured in ways closely analogous to those employed in similar measurements on electrons. Hence, from a knowledge of e, M may be computed. The mass of the electron that has been removed is negligible. A few of the various methods that have been used will be briefly described.

4-12. e/M: Parabola Method.—It was discovered by Goldstein[1] in 1886 that luminous streams appeared behind a perforated cathode in an electrical discharge in a gas at low pressure. He called these rays *Kanalstrahlen* because of the channels in the cathode through which they passed. Later investigators showed that they are composed of streams of positively charged particles closely akin to cathode rays. J. J. Thomson[2] did much of the original work on these rays, which he called *positive rays*. He made the first determination of the ratio of their charge to their mass by a method very similar to that used by Kaufmann for β rays. Figure 4-14 indicates the arrangement used.

The discharge is run in a partially-evacuated tube between the anode A and the cathode C, which is pierced by a long narrow channel, so that the positive rays emerge in a fine pencil. They then pass between the condenser plates P and the poles of an electromagnet M, and strike a photographic plate S. In common with cathode rays, these positively charged particles possess the property of affecting a photographic emulsion, so if no fields are applied, a small spot is produced in the center of the plate S. When a potential difference is set up between the plates P and a magnetic field maintained parallel to the electric field, the spot is found to be spread out into a series of parabolas. The significance of these curves may be seen from an examination of the equations of motion for a particle of positive charge ne and mass M entering the fields E_z and H_z, with a velocity v_x along the x-axis. From Eqs. (4-1), (4-2), and (4-3), we have

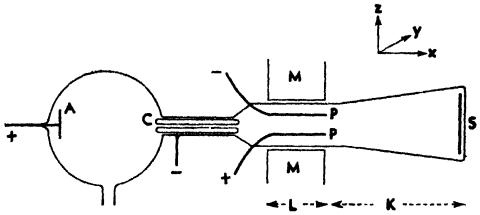

FIG. 4-14.—J. J. Thomson's parabola method for measuring ne/M of positive ions.

$$M\frac{dv_x}{dt} = nev_yH_z \tag{4-25}$$

$$M\frac{dv_y}{dt} = -nev_xH_z \tag{4-26}$$

$$M\frac{dv_z}{dt} = neE_z \tag{4-27}$$

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[1] GOLDSTEIN, *Berlin. Ber.*, **39**, 691 (1886).

[2] THOMSON, J. J., *Phil. Mag.*, **13**, 561 (1907); **20**, 752 (1910); **21**, 225 (1911); **24**, 209 (1912); "Rays of Positive Electricity," 2d ed., Longmans (1921).

From the first two of these equations we see that the path of the particles is circular in the xy plane, the radius of curvature being given by Eq. (4-10) as

$$r = \frac{v_x M}{neH_z}$$

If the fields are uniform over the length L of the plates P, and zero elsewhere, and if L is small compared to the distance K from the plates P to the photographic film, then the angular deflection θ in the xy plane is approximately given by: $\tan \theta = y/\left(K + \frac{L}{2}\right)$. We have also $\sin \theta = L/r$, so if the angle is so small that the tangent may be set equal to the sine, we find

$$y = \frac{L}{r}\left(K + \frac{L}{2}\right)$$

or, on substituting for r from the equation above,

$$y = \frac{L\left(K + \frac{L}{2}\right)ne}{v_x M} H_z \tag{4-28}$$

If we integrate Eq. (4-27) over the time required for the particles to pass through the condenser plates and replace this time by L/v_x, we obtain

$$v_z = n\frac{e}{M}E_z\frac{L}{v_x}$$

The angular displacement in the xz plane is given by

$$\tan \phi = \frac{z}{\left(K + \frac{L}{2}\right)} = \frac{v_z}{v_x}$$

where z is the displacement in the z direction on the film. Hence

$$z = \frac{L\left(K + \frac{L}{2}\right)ne}{v_x^2 M} E_z \tag{4-29}$$

Eliminating v_x from Eqs. (4-28) and (4-29), we find as the equation of the trace on the photographic plate

$$y^2 = \frac{neH_z^2}{ME_z}\left(K + \frac{L}{2}\right)Lz \tag{4-30}$$

where H and E are both expressed in electromagnetic units. Thus for a constant value of ne/M particles of all velocities lie on this parabola. The solid lines in Fig. 4-15 represent the traces of particles with two different values of ne/M. The length of the parabola described depends on the range of velocities present among the ions in the beam. The fact that the parabola is sharply defined shows that the values of ne/M of the ions giving rise to a parabola are all the same. If the magnetic field is reversed, halfway through the exposure, the parabolic traces shown as dotted lines in the figure also appear. This is generally done as it facilitates the measurement of the plate. The simple expression, Eq. (4-30), is not applicable for accurate work, as the assumption of constant electric and magnetic fields over the distance L is not justified. More accurate expressions are developed in the treatises on this subject. Using this method, J. J. Thomson measured the masses of the atoms and molecules of many gases, and in 1912 he made the first discovery of isotopes not belonging to radioactive substances by recording the two parabolas formed by neon. These have the atomic weights of 20 and 22 on the basis of oxygen as 16.

As can be seen from Eq. (4-30), it is the value of ne/M which is given by the parabolas, so that n must be known if M is to be determined. The general principle upon which we may proceed is that when we choose the proper value of n, the masses of the ions must be approximately equal to those determined electrolytically from a knowledge of Faraday's laws, the atomic weight, and Avogadro's number. Thus if hydrogen is present in the discharge tube, we obtain two strong parabolas, one having a ratio of ne/M equal to twice that of the other. The larger of these corresponds very closely to the value of e/M obtained for the hydrogen ion in electrolysis. Hence the ions giving rise to this parabola are either H^+ or H_2^{++}, and the two parabolas represent either the singly charged atom and molecule or the singly and doubly charged molecule. Thus on our knowledge that hydrogen is normally a diatomic gas, and upon the assumption of small integral values for n, we have the two possibilities represented by cases A and B:

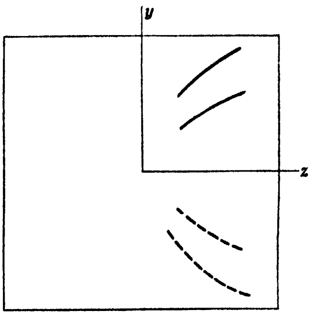

FIG. 4-15.—The parabolas obtained by the Thomson method. Each curve represents a single value of ne/M, ions of different velocities falling on different parts of the curve. The dotted parabolas are formed when the magnetic field is reversed.

Case A	Case B
H^+	H_2^{++}
H_2^+	H_2^+

It is highly doubtful if the doubly ionized molecule H_2^{++} would be at all stable, so that Case B is in all probability excluded and we may conclude that Case A is the one which actually exists. This conclusion, that the ions formed in hydrogen have the same charge but different masses, is confirmed by the presence of a third parabola under certain conditions. The value of ne/M for this parabola is one-third of the larger ne/M of the other two. The interpretation of the three ions on the basis of the two schemes *A* and *B* would have to be:

Case *A*	Case *B*
H^+	H_2^{++++++}
H_2^+	H_2^{+++}
H_3^+	H_2^{++}

Hence Case *B* must be ruled out, representing as it does an impossible series of charges. Thus these hydrogen ions are the singly charged monatomic, diatomic, and triatomic molecular ions. By comparison with the ions formed in another gas, such as helium, it may also be shown that case *B* represents absolute values of ne/M which are not observed.

Positive-ray analysis is one of the most useful tools for the investigation of atomic and molecular structures. More accurate methods than the positive-ray parabolas of Thomson have been developed, and these will now be considered briefly.

4-13. e/M: Mass Spectrograph of Aston.—This instrument, shown schematically in Fig. 4-16 was devised by Aston[1] for the accurate measurement of the masses of positive ions. Its chief advantage over the parabola method lies in the property of the instrument to bring to a single focus ions of all velocities having the same value of ne/M, the focal points for different values of this ratio being distributed almost linearly along a photographic plate.

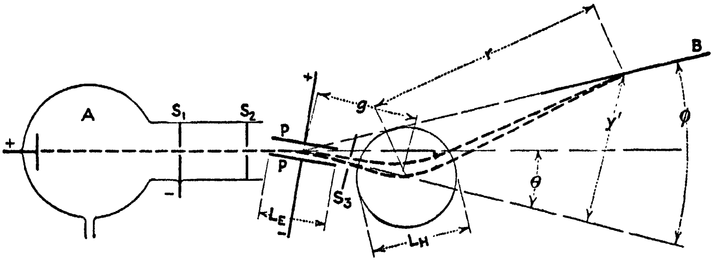

FIG. 4-16.—Aston's mass spectrograph for measuring ne/M of positive ions.

Positive ions from some suitable source in a bulb *A* pass through the slits S_1 and S_2, say, along the positive x-axis, and enter the region between the condenser plates *P* which are of length L_E. Here they are deflected by the electric field *E* through a small angle θ, given by Eq. (4-4), wherein we put tan θ equal to θ, and obtain

$$\theta = \frac{neE}{Mv^2}L_E \tag{4-31}$$

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[1] ASTON, *Phil. Mag.*, **38**, 709 (1919); "Isotopes," 2d ed., Longmans (1924); *Proc. Roy. Soc.*, **115**, 487 (1927); **126**, 511 (1930).

Here v is the velocity of the particular ion considered, as it leaves S_2. The ions then pass through the magnetic field H, perpendicular to their motion and to the electric field, applied in such a sense as to give them a deflection opposite to that due to the electric field. If we now adopt a new set of axes, with x' along the direction of motion of the ions as they enter the magnetic field, then $y'/r = \tan\phi \cong \phi$, where ϕ is the angular and y' the linear deflection caused by the magnetic field, and r is the distance from the center of this field to the point on the photographic plate where these ions come to a focus. This deflection may be taken from Eq. (4-28), if we replace $\left(K + \frac{L}{2}\right)$ by r, and we find

$$\phi = \frac{neH}{Mv} L_H \tag{4-32}$$

where L_H is the length of the path of the ions in the magnetic field, approximately the diameter of the field, since the deflection is small. Eliminating v from Eqs. (4-31) and (4-32) we obtain

$$\frac{ne}{M} = \frac{E\phi^2 L_E}{H^2 \theta L_H^2} \tag{4-33}$$

where θ and ϕ can be calculated from the location of S_3 and the trace on the photographic plate.

The optimum position of this plate is given by a consideration of the focusing property of the instrument. Focusing is accomplished when the diverging rays from S_3, of different velocities but the same value of ne/M, are brought together by the magnetic field, as shown in Fig. 4-16. For a small difference, dv, in the velocity of two ions, the difference of their deflection in the electric field is given by differentiating Eq. (4-31) with respect to v:

$$d\theta = -\frac{2neEL_E}{Mv^3} dv$$

The difference in deflection in the magnetic field is found by differentiation of Eq. (4-32):

$$d\phi = -\frac{neHL_H}{Mv^2} dv$$

Dividing the first of these equations by Eq. (4-31) and the second by Eq. (4-32), and comparing the results, we see that

$$\frac{d\phi}{\phi} = \frac{1}{2}\frac{d\theta}{\theta}$$

If the distance from the center of the plates P to the center of the magnetic field is g, and if the distance from this last point to the focus on the photographic film for ions of this ne/M is r, then the spreading of ions of different velocities due to the electric field is $(r + g)d\theta$, and the convergence due to the magnetic field is $r d\phi$. The condition of focus is for these two effects to annul each other, *i.e.*,

$$(r + g)\, d\theta = r\, d\phi$$

or

$$\frac{(r + g)}{r} = \frac{d\phi}{d\theta} = \frac{\phi}{2\theta}$$

from the equation above. Therefore

$$\frac{r}{g} = \frac{2\theta}{\phi - 2\theta}$$

This is the equation of the line which is the locus of the focal points for different values of ne/M in polar coordinates. It may be transformed into Cartesian coordinates, with the x-axis along the original direction of motion of the ions through S_1 and S_2, and the y-axis passing through the center of the plates P, by the substitutions (if θ and ϕ are small)

$$x = g + r \quad \text{and} \quad y = -g\theta + r(\phi - \theta)$$

The polar equation then becomes

$$y = \theta x \tag{4-34}$$

Therefore, when the photographic plate lies along this line, the ions of various values of ne/M come to their respective foci on the plate with very sharp images. The resolving power of the mass spectrograph of Aston is such that measurements of ionic masses are made with an accuracy of 1 part in 10,000, while the resolving power is 1 in 600. The details of the experimental procedure are fully described in the references which have been given.

4-14. *e/M*: Method of Dempster.—A third method of measuring the ratio of the charge to the mass of positive ions is due to Dempster.[1] It is essentially similar to that used by Classen[2] for electrons. Since it also possesses focusing properties, it is capable of the same order of precision as Aston's apparatus. In general, electrical rather than photographic recording is used. Many forms of the apparatus have been designed, and the particular form depends on the purpose for which it is intended. For the investigation of the ratio of the charge to the mass of positive ions, the design shown schematically in Fig. 4-17 is satisfactory. Positive ions from a suitably prepared filament F are drawn toward the slit S_1 by a potential difference V between F and S_1. The region above this slit is shielded from the strong magnetic field H existing over the box-like region M. When the ions enter this latter space, which is free of electric fields, they are bent into a circular path of radius r given by an expression analogous to Eq. (4-10). Those ions that have the proper ratio of charge to mass then pass through the slit S_3, and their charge, on entering the collector C, is recorded by an electrometer. The focusing property is indicated by the dotted lines in Fig. 4-17, which represent the paths followed by ions entering S_1 at angles $\pm\alpha$ with the central beam. The points O, O_1, and O_2 represent the mid-points of the diameters of the three circular paths which coincide at S_1. If x is measured along the line S_1S_3, then the length of this line intercepted by the central beam is $2r$, while for the two extreme beams it is $2r - dx$, where $dx = 2r - 2r \cos \alpha = 2r(1 - \cos \alpha)$, as may be seen from the geometry of the figure. If α is small,

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[1] DEMPSTER, *Phys. Rev.*, **11**, 316 (1918); *Proc. Nat. Acad. Sci.*, **7**, 45 (1921); *Phys. Rev.*, **18**, 415 (1921); **21**, 209 (1923).

[2] CLASSEN, *Jahrbuch d. Hamburg. Wiss. Anst.*, **25** (1907); *Physik. Zeits.* **9**, 762 (1908).

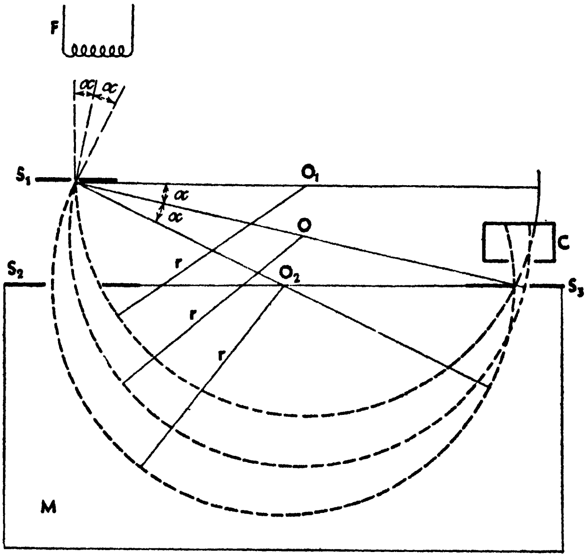

FIG. 4-17.—Dempster's mass spectrograph for measuring ne/M of positive ions. The angles α have been greatly exaggerated in the sketch in order to bring out the focusing property. The ions' paths between S_1 and S_2 are actually almost straight lines, due to nearly perfect shielding from the magnetic field in this region.

$$\frac{dx}{r} = \alpha^2$$

Thus an angular spread of the beam of 3° on either side of the mean produces a widening of the beam at S_3 of less than 0.01 cm., if the radius is 3 cm. The focus is at its best when the path is a semi-circle. The resolution may be calculated from the relation analogous to Eq. (4-11)

$$\frac{ne}{M} = \frac{2V}{r^2H^2} \tag{4-35}$$

On differentiating and then substituting from this equation, we obtain

$$\frac{dM}{M} = 2\frac{dr}{r}$$

For a slit width, at S_3, of 0.02 cm., and a radius of 3 cm., the resolving power is therefore about 1 per cent.

The construction and method of use are discussed in the papers by Dempster which have been referred to. As the ions are detected electrically rather than photographically, it is easier to make quantitative estimates of their relative intensities, than with the Aston mass spectrograph.

The impression must not be left with the reader that the accuracy of a mass spectrograph is limited by the several geometrical approximations that have been made in deriving Eqs. (4-33) and (4-35), nor on the limit of accuracy with which a magnetic field can be determined with a search coil. The mathematics of the instruments are of interest in that they explain why they work at all, but precision measurements of ionic masses are actually performed by empirical methods that do not depend on precise knowledge of the geometry of the apparatus or on the exact value of the magnetic field.

In principle, the method is simply that of interpolating the atomic weight of an unknown ion from the relative position of its trace on the photographic plate with that left by oxygen, the atomic weight of which is 16 by definition. If electrometer recording is used, as in the Dempster instrument, a record of the accelerating potentials takes the place of distances along the photographic plate. The magnetic field is held at some fixed though unknown value by keeping a constant current flowing in the magnet coils. Electric fields and accelerating potentials may be found very accurately with a good voltmeter. For the details of the various methods of calibrating a mass spectrograph and of determining atomic weights by "coincidence" and by "brackets," the reader is referred to the work of Aston.

4-15. e/M: Electrostatic Methods.—Two other methods of measuring the ratio of the charge to the mass of positive ions may be mentioned briefly. These do not depend on magnetic deflection and are quite closely analogous to the means discussed for determining e/m of electrons.

The velocity filter was first adapted for use with positive ions by Hammer,[1] and has been used subsequently by W. R. Smythe.[2] The method is inherently capable of great accuracy, but so far no particularly significant results have been obtained with it.

A very interesting space-charge procedure has been discovered by Kingdon.[3] From the natural period of oscillation of a positive ion located in the potential minimum, due to space charge, outside a surface that is emitting electrons, the ratio of ne/M for the ion can be calculated. This scheme has not as yet been rendered a precision method, but its possibilities are of considerable interest.

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[1] HAMMER, *Physik. Zeits.*, **12**, 1077 (1911).

[2] SMYTHE, W. R., *Phys. Rev.*, **28**, 1275 (1926).

[3] KINGDON, *Phys. Rev.*, **33**, 1075 (1929).
KINGDON and CHARLTON, *Phys. Rev.*, **33**, 998 (1929).

4-16. Experiment on the Measurement of e/M.—The construction and operation of a simple apparatus which may be used for the analysis of positive ions by the Dempster method will be described. The instrument indicated in Fig. 4-18 may be used to investigate positive ions both from the filament F, when it is impregnated with a salt such as Al_2PO_3, or those formed by electron bombardment in the gas near the grid. When a gas is to be used, it is necessary to employ a rapid pumping system, so that a reasonably large pressure gradient can be maintained between the regions on the two sides of slit S_1. Under these circumstances, ions may be formed readily in the region above S_1 and will suffer comparatively few collisions with other molecules or atoms while passing through the magnetic field, and so reach S_3 with little loss in intensity. For this purpose, S_1 should be very narrow, of the order of 0.01 cm., and the vacuum connections should be as short as possible between the apparatus and the pumps. When ions emitted from the filament are to be analyzed, a high vacuum is maintained in the entire apparatus and the procedure is less difficult.

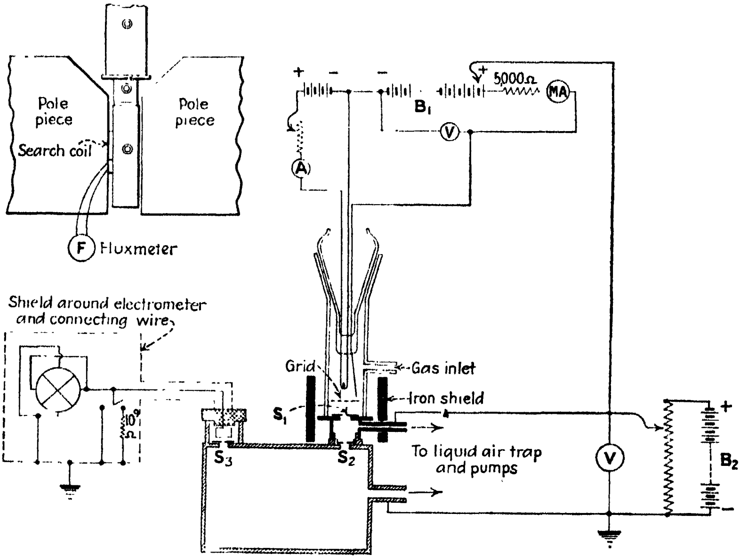

FIG. 4-18.—A Dempster type of apparatus for measuring ne/M of positive ions.

The positive-ion box is constructed of two iron plates 3 by 2 by $\frac{1}{8}$ in., which form the walls perpendicular to the magnetic field, and four pieces of brass strip $\frac{1}{2}$ in. wide and $\frac{1}{8}$ in. thick. These parts are both screwed and soldered together to make them vacuum tight. Two holes 1 cm. long and 0.2 cm. wide are cut in the top of the box, 6 cm. apart. Adjustable knife edges are screwed over one of these, to form slit S_3, and a short length of ½-in. brass tube is soldered around it to carry the bakelite plug which supports the Faraday collector. This is in the form of a small cylindrical box with a 0.2-cm. slit along one of its face diameters. Such an arrangement prevents the loss of ions by reflection. As the positive-ion box is at ground potential, provision for a guard ring is unnecessary.

Around the edges of the other slit S_2, a brass collar ⅛ in. high is soldered, in order to hold in place an insulating ring of bakelite. The outside of the latter is turned to fit snugly the ½-in. iron tube about ⅝ in. long which supports a circular iron plate. A channel is turned in this plate into which is waxed the glass tube that holds the filament and grid. The plate has a hole cut in it, 1 by 0.2 cm., over which are screwed the adjustable knife edges of slit S_1. The iron tube has a metal pipe let into it, for the vacuum connection, and another pipe is built into the side wall of the positive-ion box for a similar purpose.

Numerous variations have been found equally satisfactory. Mica or cellophane instead of bakelite may be used as an insulator. The slit S_1 may be in metallic contact with the main box if an additional grid is introduced above it, although this has certain disadvantages. The adjustment of the slits S_1 and S_3, so that they are parallel to one another and also perpendicular to the sides of the box, may be made conveniently with a cathetometer.

A glass tube about 1½ in. in diameter is waxed into the channel in the plate supporting S_1. A gas inlet is in the side of this tube, which terminates at its upper end in a ground glass joint, sealed with wax, supporting the filament and grid. If a very heavy filament current is used, it may be necessary to cool these joints with a cooling coil or an air blast. The grid is a coarse copper or nickel gauze supported by a metal ring. The filament is generally in the form of a fine spiral of 5-mil tungsten wire; this is a very convenient source of electrons, and it is easy to dope for the emission of positive ions.

The apparatus is supported between the poles of an electromagnet capable of producing a fairly uniform field of several thousand gauss over the volume of the box. For convenience the pole pieces may be cut away as indicated in the sketch. The magnetic field is measured in the usual way with a search coil and ballistic galvanometer or fluxmeter. The throws for a series of complete reversals of the current in the coils are noted and the field is calculated from the constants of the search coil and the galvanometer. The most satisfactory procedure is to adjust this field to a convenient value, which may be roughly calculated when the type of ion to be investigated is known, and then to keep this field constant, while the electric potentials are varied.

The intensities of the ion beams obtainable with such an apparatus are fairly large, so that an electrometer with a sensitivity of about 1,000 mm. per volt is a satisfactory recording instrument. With a shunt resistance of about 10^9 ohms across the electrometer, the constant-deflection method may be employed. The electrometer and the connection to it from the Faraday collector must be well shielded. Further details of electrometer technique are given in Appendix A.

The functioning of the apparatus is much improved if the region above S_2 is shielded from the magnetic field. This may be conveniently accomplished by cutting a piece of iron pipe lengthwise, making semicircular holes in the two halves to admit the vacuum connection and placing the two pieces about the lower part of the filament and slit units, as shown in the figure.

If positive ions emitted from the filament are to be studied, the electrical connections are simpler than those indicated in Fig. 4-18, where the set-up is for ion formation by electron bombardment. A potential difference of 50 to 100 volts is produced by a battery or generator between the filament and grid, the latter being negative with respect to the former in order to insure a copious emission from the filament. A protective resistance of a few thousand ohms and a galvanometer for measuring the emission should be included in this circuit. The grid is connected to the slit S_1 so that the region in between them is field free, and the main accelerating potential is applied between S_1 and S_2. This potential is varied by means of a potentiometer and may be reversed in direction if very slow ions are desired. The total potential through which the ions fall is given by the algebraic sum of the two applied potentials. The ions so obtained are generally singly charged.

The material to be used on the filament depends on the type of ion desired. The salts that emit positive ions on being heated are discussed by Richardson[1] and in the literature pertaining to this subject.[2] A series of sources which emit ions of the alkali metals are described by Kunsman.[3] The following minerals, pulverized and applied to the filament with varnish, will emit the ions indicated:

Spodumene	Li^+
Jadite	Na^+
Leucite	K^+
Pollucite	Cs^+

Such filaments will last for a period of several hours without recoating. It is also possible to obtain caesium ions, for instance, by simply having caesium vapor present in the region surrounding the filament. Caesium atoms which strike the filament lose an electron, and the resulting ion is drawn away by the field.

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[1] RICHARDSON, "Emission of Electricity from Hot Bodies," Longmans (1916).

[2] MARX, *Handbuch d. Radiologie*, Akad. Verlag. Gesell. Leipzig, **4**, 220 (1927).

[3] KUNSMAN, *Science*, **62**, 269 (1925).

When a gas is to be used in the apparatus, the electrical connections may be made as shown in Fig. 4-18. The filament is simply a tungsten spiral, heated in the usual manner, and electrons emitted by it are accelerated to the grid by the battery B_1, which may be of about 100 volts. This potential may be varied with a potentiometer across the battery or simply by clipping on to individual cells. A protective resistance and milliammeter (for recording the thermionic emission) should be included in the circuit. The slit S_1 is made a few volts negative with respect to the grid, so that ions formed by collision of the electrons with gas atoms or molecules between the grid and S_1 will move toward S_1. The main accelerating potential, controlled by a potentiometer across the battery or generator, is applied between S_1 and S_2. For very light ions, such as H^+ and H_2^+, a potential of 200 or 300 volts should be available. The small field between the grid and S_1 introduces some inaccuracy, for it is not known at what point in this region the ions were formed, but it generally increases the intensity of the ion beam entering the analyzer. This potential may be made small enough so that the uncertainty in V is of the order of 1 per cent.

Gas is admitted slowly into the region of the filament and is pumped out as rapidly as possible from below S_1. Artificial leaks, which may be employed to admit the gas from its reservoir, are described in Appendix B. The pressure may be varied by altering either the artificial leak or the back pressure in the reservoir; it may be measured with a McLeod gauge. With a 0.01-cm. slit at S_1, pressures of 10^{-2} to 10^{-4} mm. Hg above the slit will give satisfactory results, if rapid pumping from the exits is provided. When the pressure conditions have been adjusted, the procedure is the same as in the case of ions emitted from the filament. The electrometer deflections are recorded, as the accelerating potential of the ions is varied. Since the mass of the ion is inversely proportional to the voltage, a plot of the deflections against the reciprocal of the voltage gives a curve which shows the relative abundance of the various types of ions as a function of their masses. A typical graph is shown in Fig. 4-19. With the magnetic field and the radius of curvature known, the ions may be identified.

The resolving power may easily be made sufficient to separate any isotopes present for elements with atomic weights less than 50. Even though wide slits are used, the presence of the two lithium isotopes (Li_6 and Li_7) is readily detected, using a spodumene-coated filament. In addition, the apparatus may be used to investigate various other phenomena in connection with ions. From a variation of the accelerating potential of the electrons, fairly accurate determinations may be made of the voltages at which different types of gas ions appear. Comparatively unstable ions, such as H_3^+, may be detected over a large range of pressure. From the change in the intensities of the peaks with pressure, the various processes of ion formation may be investigated.[1]

4-17. Determination of *R*, *N*, and *k* by Electrolysis.—From the data found with a mass spectrograph such as has been described, a great deal of additional information can be obtained by the performance of a simple experiment of electrolysis. With hydrogen in the analyzer, the mass, M_H, of the hydrogen atom and of the hydrogen molecule, M_{H_2}, has been determined in grams. If oxygen has been used, the mass of this atom and molecule has also been obtained. (The life of a tungsten filament in oxygen, even at very low pressures, is short, so the use of a platinum filament impregnated with alkaline-earth oxides is recommended.) Hence the atomic weight of hydrogen, A_H, on the arbitrary basis that the atomic weight of oxygen is 16 exactly, is given by $A_H = 16M_H/M_O$.

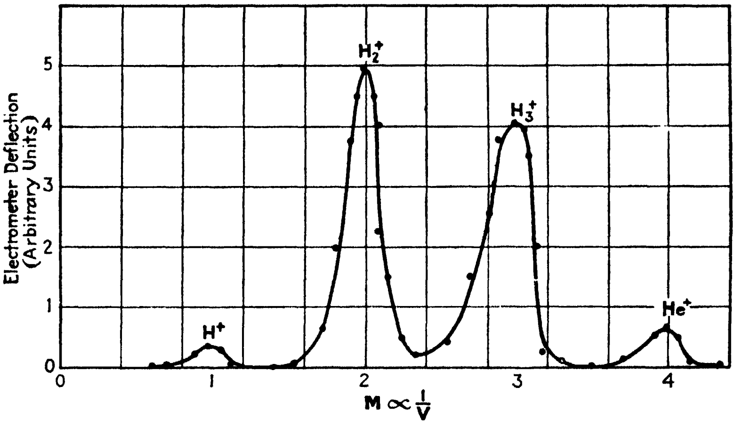

FIG. 4-19.—Typical e/M curves obtained with the Dempster type of mass spectrograph described in the text. Hydrogen containing a trace of helium was used, at a pressure of 0.01 mm. of Hg. The accelerating potential for the electrons was 30 volts.

An electrolysis apparatus is set up, the liquid being a dilute solution of an acid or a base. Hydrogen and oxygen, liberated by the passage of a current for a known time, are collected. Each atomic hydrogen ion in the electrolysis process carries a charge of e e.m.u., so that the number of hydrogen ions reaching the electrode is $n' = it/e$, where i is the current in electromagnetic units, and t the time in seconds. Since gaseous hydrogen is diatomic, the number of molecules collected is $n = it/2e$. These occupy a volume v, at a pressure p, and at an absolute temperature T, all experimentally measurable. The mass of this volume of hydrogen is $n2M_H$, so that the volume occupied by unit mass, at this pressure and temperature, is $v/(n2M_H) = ve/M_Hit$. Therefore the volume V of 1 gram-molecule of hydrogen, under these same conditions, is $V = 2A_Hve/M_Hit$, since $2A_H$ is the molecular weight of hydrogen, and a gram-molecule of a substance is its molecular weight in grams. The relation $pV = RT$ defines the quantity R, known as the *universal gas constant*, where p is the pressure in dynes per square centimeter, V the volume of a gram-molecule, and T the absolute temperature. Thus with the above experimental value of V, and measurements of p and T, R may be found, since we have already determined the value of the charge e. Loschmidt's number (the number of molecules in 1 cm.^{3} at a pressure of 76 cm. Hg and at 0°C.) may be found from the above expression for n, if the observed volume is reduced to its value at these standard conditions. Also, the observed value of v divided by V, as determined above, gives the number of gram-molecular volumes of hydrogen in the tube, so if we divide this quotient into the number of molecules present, n, we obtain the number of molecules in a gram-molecule, which is Avogadro's number N. Finally, we may calculate Boltzmann's constant k (the gas constant per molecule), for it is given by $k = R/N$.

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[1] KALLMANN and ROSEN, *Physik. Zeits.*, **32**, 521 (1931).
SMYTH, H. D., *Rev. Mod. Phys.*, **3**, 347 (1931).
WIEN and HARMS, *Handbuch der Expt. Physik*, **14** (1927).

The experimental procedure for this work is very simple and familiar. A standard electrolysis apparatus designed to collect the liberated gases may be used. A volume calibration can be made, or the existing calibration may be checked by weighing the apparatus (after it has been cleaned and dried) when it is empty and when it is filled with a volume of mercury or water equal to the volume of gas which has been collected. A convenient solution for electrolysis is a 10 per cent solution of sulphuric acid. Its density may be measured or found in chemical tables, in order to determine the gas pressure from measurements of the difference in height of the solution in the collecting tube and the reservoir, combined with the reading of a barometer. Correction should also be made for the vapor pressure of the electrolyte. This may be found by allowing a few drops of the solution to rise through the mercury column of an auxiliary barometer and by noting the depression of this column when just a little of the liquid is condensed above it.

During the electrolysis, the current should be held as nearly constant as possible by means of a series rheostat. A small current density has the advantage that only a short time need be allowed after the completion of the electrolysis for temperature equilibrium to be established, and few water droplets are carried up into the gas by the violence of the process.

4-18. Nuclear Masses.—Probably the most important result obtained by means of the mass spectrograph is the accurate measurement of the atomic weights of the elements. The development of the instrument for this purpose is due largely to Aston. Together with X-ray evidence, it has definitely established the significant sequence in which the elements occur, and, in conjunction with studies in radioactivity, it supplies a first step in the investigation of atomic nuclei.

The familiar Periodic Table of the elements is of significance for all those characteristics which depend on the structure of the outer regions of the atoms, such as chemical properties, visible spectra, etc. The classification in a sequence is of much greater importance in the study of the nuclei of atoms.

An inspection of the Periodic Table (page 451) shows that the atomic weights of the elements have nearly integral values. This suggests that all atoms are built up of integral numbers of a universal mass unit, which can be none other than the hydrogen nucleus, or so-called proton, which carries a charge equal in magnitude but opposite in sign to that of the electron. Evidence from the phenomena of radioactivity and from the artificial disintegration of the elements strongly supports this view, which was first anonymously hazarded by Prout in the *Annals of Philosophy* as early as 1815. The same evidence further suggests the existence in atomic nuclei of certain complex units. One of these is composed of one proton and one electron very closely associated with one another and is called a neutron; the other is formed of four protons and two electrons, probably as two protons and two neutrons, and is called an α particle. These complex units have great inherent stability, and though the theory of the nucleus is still in a very early stage of development we may conceive of it as made up of closely packed protons and neutrons, some of which may be associated together to form α particles. As the atom is electrically neutral, on the whole, the number of un-neutralized protons must equal the number of external electrons which are responsible for the chemical properties. Thus another quantity besides the mass is of great importance in the description of atomic structure, and this is the number of the excess positive charges on the nucleus, known as the atomic number Z. The discovery and interpretation of this quantity we owe very largely to the work of Moseley on X-ray spectra, which will be described in Chap. IX.

The mass of an electron is roughly 1/2,000 of that of a proton, so the nuclear mass will depend, to a first approximation, merely on the number of protons contained in it. If A is the number of protons (including those in neutrons and in α particles), it is approximately equal to the atomic weight, and if N is the number of neutrons in the nucleus (which is equal to the number of electrons neutralizing part of the positive charge due to the protons), then the atomic number Z is given by

$$Z = A - N \tag{4-36}$$

From various lines of evidence, some of which will be mentioned later, atomic radii are found to be of the order of 10^{-8} cm. The experi-

THE ACCURATELY KNOWN ATOMIC WEIGHTS AND PACKING FRACTIONS OF CERTAIN ISOTOPES[1]

Atomic number	Name	m_1	Atomic weight	Packing fraction
(0	Neutron	0	1.0067	+67 ± (10))*
1	Hydrogen	1	1.00778	+77.8 ± 1.5
		2	2.01363	+67.5 ± 0.9
2	Helium	4	4.00216	+ 5.4 ± 1
3	Lithium	6	6.0145	+20 ± 3
		7	7.0146	+17 ± 3
4	Beryllium	9	9.0155	+17.2 ± 0.7
5	Boron	10	10.0135	+13.5 ± 1.5
		11	11.0110	+10 ± 1.5
6	Carbon	12	12.0036	+ 3 ± 1
7	Nitrogen	14	14.008	+ 5.7 ± 2
8	Oxygen	16	16.0000 (Def.)	0
9	Fluorine	19	19.0000	0 ± 1
10	Neon	20	19.9967	− 1.9 ± 0.5
		22	21.9947	− 2.4 ± 0.4
14	Silicon	28	27.9818	− 6.5 ± 1.5
15	Phosphorus	31	30.9825	− 5.6 ± 1.5
17	Chlorine	35	34.9796	− 5.8 ± 0.3
		37	36.9777	− 6.0 ± 0.5
18	Argon	36	35.976	− 6.6 ± 1.5
		40	39.971	− 7.2 ± 1
24	Chromium	52	51.948	−10. ± 3
30	Zinc	64	63.937	− 9.9 ± 3
33	Arsenic	75	74.934	− 8.8 ± 1.5
34	Selenium	78	77.938	− 8.0 ± 2
		80	79.941	− 7.3 ± 3
35	Bromine	79	78.929	− 9.0 ± 1.5
		81	80.926	− 9.2 ± 1.5
36	Krypton	82	81.927	− 8.8 ± 1.5 (Average of 6 isotopes)
41	Niobium	93	92.90	− 8 (approx.)
42	Molybdenum	98	97.946	− 5.5 ± 2
		100	99.945	− 5.5 ± 2

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[1] ASTON, *Proc. Roy Soc.*, **115**, 487 (1927); **126**, 511 (1930); **130**, 302 (1931); **132**, 487 (1931); **134**, 571 (1932); *Nature*, **130**, 130 (1932). BAINBRIDGE, *Phys. Rev.*, **42**, 1 (1932); **43**, 378, 424; **44**, 56, 57 (1933). * See Sec. **10-15**.

THE ACCURATELY KNOWN ATOMIC WEIGHTS AND PACKING FRACTIONS OF CERTAIN ISOTOPES.—(*Continued*)

Atomic number	Name	m_1	Atomic weight	Packing fraction
50	Tin	120	119.912	-7.3 ± 2
52	Tellurium	128	127.935	-5 ± 2
53	Iodine	127	126.932	-5.3 ± 2
54	Xenon	134	133.929	-5.3 ± 2
55	Caesium	133	132.917	-5.0 ± 2
56	Barium	138	137.916	-6.1 ± 2
73	Tantalum	181	180.89	-4 (approx.)
75	Rhenium	187	186.981	-1 ± 2
76	Osmium	190	189.981	-1 ± 2
		192	191.981	-1 ± 2
80	Mercury	200	200.016	$+0.8 \pm 2$
81	Thallium	205	204.978	$+1.8 \pm 2$

Packing fraction, $f = \frac{m - m_1}{m_1} \times 10^4$. m = mass in atomic weight units.

m_1 = number of protons and neutrons.

ments of Rutherford and others on the scattering of α particles by matter indicate that nuclear radii are of the order of 10^{-12} cm. This is probably of the same order of magnitude as the effective region of influence or radius of an electron. Thus the atomic system is in all probability a very open one, and therefore problems dealing with the external structure of the atom are of an entirely different type from those arising in connection with the constitution of the very small and enormously dense nucleus. The experimental evidence for a theory of the nucleus is at present rather meager and inaccurate, but the problems to be solved are of the greatest fascination and constitute one of the most active fields of modern speculation and research. The lines of attack are chiefly through radioactivity. As there is here no space for an adequate discussion of the present situation of our knowledge of the nucleus, the reader is referred to the treatment of Gamow[1] and the footnotes in Sec. **10-15**.

From measurements of the type indicated in this chapter it has been shown that the mass of a hydrogen atomic nucleus is 1.6609×10^{-24} gram while that of an electron is 9.035×10^{-28} gram. The measured mass of the helium nucleus is 6.598×10^{-24} gram and there is abundant evidence that it is composed of four protons and two electrons (two protons and two neutrons) grouped together in the stable configuration known as an α particle. We should therefore expect the mass of the helium nucleus to be $4 \times (1.6609 \times 10^{-24}) + 2 \times (9.035 \times 10^{-28}) = 6.645 \times 10^{-24}$ gram. Hence an amount of mass equal to $(6.645 - 6.598) \times 10^{-24} = 0.047 \times 10^{-24}$ gram has disappeared in the process of packing closely together the constituent parts of an α particle. On the basis of the relativistic equivalence between mass and energy, $E = mc^2$ [Eq. (1-31)], we see that this corresponds to the liberation of 4.23×10^{-5} erg for each α particle formed. It is also possible to make an estimate of the mass of a neutron by a method which will be described later (Sec. **10-15**). This yields a value of 1.6600×10^{-24} gram. The difference between this value and the mass of one proton and one electron (1.6618×10^{-24} gram) is 0.0018×10^{-24} gram or 1.6×10^{-6} erg which is the energy liberated at the formation of a neutron. Thus neutrons and α particles represent systems of much less potential energy than their separate components. This fact explains their great inherent stability and their presence in atomic nuclei as building stones almost as fundamental as the proton.

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[1] GAMOW, "Constitution of Atomic Nuclei and Radioactivity," Oxford University Press (1931).

The masses of the isotopes of a great many of the other elements have also been determined to the required degree of accuracy for the calculation of the decrease in mass that accompanies their formation from the elementary particles. As a result, it is possible to calculate the packing energy or relative inherent stability of the different types of nuclei. For a fuller discussion of these concepts and comparison of the results with those from other lines of evidence, such as relative abundance and artificial disintegration, reference should be made to Gamow's book.

CHAPTER V

THE WAVE ASPECT OF MATTER

5-1. De Broglie Waves.—During the first two chapters certain of the crucial experiments dealing with electromagnetic waves or photons were discussed. It was seen that these experiments were capable of description from either a wave or particle point of view. The chief experimental foundations of the electromagnetic wave theory, such as the phenomena of interference, diffraction, and polarization, are of the most convincing nature, but a discussion of them lies more properly in the field of physical optics. On the other hand, the more recently discovered phenomena of the photoelectric effect, the Compton effect, and others which have to do with the emission and absorption of radiation, point unequivocally to a particle or photon conception of radiation. This resulting dualism may be reconciled, at least from a conceptual point of view, by the assumption that the electromagnetic wave field acts as a structure which guides the motion of the energy-carrying photons, as outlined at the end of Chap. II.

The introduction to the study of elementary material particles in the last two chapters has followed a very different course. Their properties of charge and mass which we have so far considered involve only simple extensions of the concepts which are already familiar in our experience of matter on a large scale. While these properties are of fundamental importance they are not the only known attributes of electrons, protons, and atomic systems. In later chapters we shall see that the ability of these particles to react with radiation and the magnetic moments associated with them present many of the most interesting problems of atomic physics. We shall first consider the recent revolutionary experiments of Davisson and Germer[1] followed by the confirmatory work of Thomson[2] and of Rupp[3] which have shown that electrons are scattered from crystals or gratings very much as if they were waves rather than particles. As a result of these observations and certain earlier theoretical work we are led to associate a wave field with these ultimate units of matter, which introduces into our conception of electrons, for instance, a wave-particle dualism in very close analogy with that which has been brought out in the discussion of photons. This is reconciled in a very similar manner, and our present point of view is that a phantom or virtual wave structure determines the path of a material corpuscle in much the same way in which electromagnetic waves guide photons. These so-called phase waves or matter waves differ in several respects from electromagnetic waves, but they also exhibit certain striking points of similarity, particularly in their ability to produce the diffraction effects by which they were discovered.

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[1] Davisson and Germer, *Phys. Rev.*, **30**, 705 (1927); *Proc. Nat. Acad. Sci.*, **14**, 317, 619 (1927).

[2] Thomson, G. P., *Proc. Roy. Soc.*, **117**, 600 (1928); **119**, 651 (1928).

[3] Rupp, *Ann. Physik*, **85**, 981 (1928).

The initial step in the wave theory of matter was taken by de Broglie,[1] when he associated a characteristic wave motion with every material particle. The possibility of such an association had been established by Sir William Hamilton[2] as early as 1828 in his treatment of the motion of mechanical systems. De Broglie's application, however, included the ideas which had previously been of such great importance in the quantum theory. For a photon, the assumption had been made that the momentum p and the total energy E (also the kinetic energy, since there is no potential energy) are given by

$$p = \frac{h\nu}{c} = \frac{h}{\lambda} \tag{5-1}$$

$$E = h\nu \tag{5-2}$$

In an analogous manner, the wave length λ, frequency ν, and velocity w, of the phantom wave associated with a particle of momentum p are given by

$$p = mv = \frac{h\nu}{w} = \frac{h}{\lambda} \tag{5-3}$$

the kinetic energy being

$$E - U = mc^2 = h\nu = \frac{hw}{\lambda} \tag{5-4}$$

where E is the total and U the potential energy of the particle, mc^2 being the relativistic expression for the kinetic energy, as given by Eq. (1-31). At the moment we do not know the connection between the phase velocity, w, of the waves and the velocity of the particle, v. We expect the phantom waves to obey a wave equation similar to that given in Chap. I for electromagnetic waves:

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} - \frac{1}{w^2}\frac{\partial^2\Psi}{\partial t^2} = 0 \tag{5-5}$$

where Ψ is the wave amplitude and w the phase velocity. Ψ depends on both space and time; we shall assume that a solution of the above equation can be written in the form $\Psi = \psi(x,y,z)\,\phi(t)$. Let us first consider the material analogue of a monochromatic wave and assume a combination sine and cosine solution:

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[1] De Broglie, Dissertation, Masson, Paris (1924); *Phil. Mag.*, **47**, 446 (1924).

[2] Hamilton, *Trans. Irish Acad.* (1828–1837); *Phil. Trans. Roy. Soc.*, **124**, 247 (1834); **125**, 95 (1835).

$$\phi(t) = \cos 2\pi\nu t + i \sin 2\pi\nu t = e^{2\pi i\nu t}$$

Substituting in the differential equation and remembering that $\lambda\nu = w$, we obtain

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{4\pi^2}{\lambda^2}\psi = 0 \tag{5-6}$$

By Eq. (5-3), using the relativity expression for the mass, Eq. (1-26),

$$\frac{1}{\lambda^2} = \frac{m^2v^2}{h^2} = \left(\frac{m_0{}^2}{1 - \frac{v^2}{c^2}}\right)\frac{v^2}{h^2} = \frac{m_0{}^2}{h^2}\left(\frac{v^2c^2}{c^2 - v^2}\right) \tag{5-7}$$

and similarly we have by Eq. (5-4)

$$\frac{m_0c^2}{\sqrt{1 - \frac{v^2}{c^2}}} = E - U$$

Squaring this and solving for v^2, we find

$$v^2 = c^2\left[1 - \frac{m_0{}^2c^4}{(E - U)^2}\right]$$

Using this in Eq. (5-7) to eliminate v^2, we obtain after a bit of cancellation,

$$\frac{1}{\lambda^2} = \frac{(E - U)^2 - m_0{}^2c^4}{h^2c^2}$$

Therefore Eq. (5-6) may be written

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{4\pi^2}{h^2c^2}[(E - U)^2 - m_0{}^2c^4]\psi = 0 \tag{5-8}$$

This expression may be simplified for the case of slowly moving particles, where relativity can be neglected. Since the non-relativistic total energy E' equals the relativistic total energy E minus the rest energy m_0c^2, we may write

$$[E - U]^2 = [m_0c^2 + (E' - U)]^2 = m_0{}^2c^4 + 2m_0c^2(E' - U) + (E' - U)^2$$

Inasmuch as the last term in this expression is equal to $(\frac{1}{2}mv^2)^2$, we may neglect it when the expression is substituted in Eq. (5-8) because of the c^2 occurring in the denominator. We therefore have

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2m_0}{h^2}(E' - U)\psi = 0 \tag{5-9}$$

Equations (5-8) and (5-9) are the so-called Schrödinger[1] wave equations—the general starting point for problems to be solved by wave mechanics. The wave amplitude ψ is, roughly speaking, a measure of the probability of finding the particle at any given point in space, so that integration of the equation, when some appropriate form of the potential energy is assumed, gives the probability locus of the particle. (Strictly, this probability is given by the square of the absolute magnitude of ψ, which is generally a complex scalar quantity.) In many cases, as when applied to atomic systems, such integration is unnecessary, and it is required merely to find what can be the possible values of the energy E such that ψ is everywhere finite and continuous. This yields, as we shall see in Chap. VII, the concept of stationary energy states, in conformity with the results of the older quantum theory but without the arbitrariness that was so characteristic of it. Detailed applications of the Schrödinger equation to various atomic problems can be found in the treatments of Schrödinger,[1] Condon and Morse,[2] Ruark and Urey,[3] Sommerfeld[4] and Mott.[5]

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[1] SCHRÖDINGER, *Ann. Physik*, **79**, 361, 489, 734 (1926); *Phys. Rev.*, **28**, 1049 (1926).

Since the position of the particle is given by the region wherein ψ has a value other than zero, it is obvious that the wave train must be finite in length if the particle is to be located within a finite region. Such a finite wave train can be represented, after the manner of Fourier's theorem, by a set of superimposed monochromatic wave trains of infinite extent, their wave lengths differing slightly from the average value λ. These Fourier components are out of step with each other except in the locality of the particle; the resultant wave amplitude ψ therefore drops rapidly to zero in both directions, before and behind.

The probability of observing the particle has a negligible value everywhere except in the range where the phantom waves are more or less in phase, *i.e.*, where the group of waves has a maximum. We are thus led to the same concept of group velocity of phantom waves as was discussed apropos the velocity of light in Chap. I. There we saw that any light signal, since it has a beginning and an end, must be described as a Fourier series of waves of slightly different wave length, which travel with different velocities if the medium is dispersive, so that the group velocity of the waves, or the velocity of propagation of the signal, is different from the phase velocity of the component waves, as shown by Eq. (1-19). The group and phase velocities coincide only if the medium is non-dispersive. For the phantom waves associated with a material particle, the particle itself corresponds to the signal or energy carrier, and it must lie within the region of reinforcement of the component phase waves; *i.e.*, the velocity of the particle is equal to the group velocity of the waves, as may be shown in the following manner. Using Eq. (1-19), the group velocity is given by

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[1] SCHRÖDINGER, "Collected Papers on Wave Mechanics," Blackie (1928).

[2] CONDON and MORSE, "Quantum Mechanics," McGraw-Hill (1929).

[3] RUARK and UREY, "Atoms, Molecules, and Quanta," McGraw-Hill (1930).

[4] SOMMERFELD, "Wave Mechanics," Methuen (1930).

[5] MOTT, "An Outline of Wave Mechanics," Cambridge University Press (1930).

$$u = \frac{d(w/\lambda)}{d(1/\lambda)} \tag{5-10}$$

where w is the phase velocity and λ the wave length of the component-matter waves. By Eq. (5-4), $w/\lambda = mc^2/h$, and by Eq. (5-3), $1/\lambda = mv/h$. Hence

$$u = \frac{d(mc^2/h)}{d(mv/h)} = \frac{d(mc^2)}{d(mv)}$$

or

$$u = \frac{d(mc^2)}{dv}\,\frac{dv}{d(mv)} = m_0c^2\frac{d\left(1 - \frac{v^2}{c^2}\right)^{-\frac{1}{2}}}{dv}\;\frac{1}{m_0\dfrac{d\left[v\left(1 - \frac{v^2}{c^2}\right)^{-\frac{1}{2}}\right]}{dv}}$$

since $m = \dfrac{m_0}{\left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}}}$, by Eq. (1-26). We have inverted the last term for convenience. Performing the indicated differentiation and canceling, we find

$$u = v \tag{5-11}$$

or the group velocity u of the phantom waves is equal to the particle's velocity v. (The same result is obtained if we use the non-relativistic expression for the kinetic energy.) Furthermore, from Eqs. (5-4) and (5-3) we have

$$h\nu = mc^2 \quad \text{and} \quad h\nu = mvw$$

so that

$$vw = c^2 \tag{5-12}$$

This shows the relation between the phase and group (or particle) velocities. We know that the particle velocity v can range from zero to c, this limit being set by relativity, and consequently the phase velocity w must range from infinity to c. The fact that this velocity of the matter waves exceeds c is not contradictory to the principle of relativity, since no signal or energy is transmitted with that speed; such quantities go with the group velocity.

5-2. The Heisenberg Uncertainty Principle.—Since the phenomenon exhibited by a group of electromagnetic waves has been seen (Chap. I) to allow us to localize the extent of any finite light signal (which in the limit would be composed of a single quantum), the position of a single material particle can be specified in an analogous manner by the resultant group of a set of phantom waves. (One monochromatic wave of infinite extent would not locate the particle at all.) We may therefore take over the group-velocity expression of Eq. (1-18) and apply it to the matter waves, to discover to what extent a definite prediction of the particle's position can be made. For simplicity, as when deriving Eq. (1-18), we shall consider but two Fourier components, since the results are the same in principle as if an infinite number of components were assumed (which is necessary if but a single resultant group maximum is to be obtained.) The amplitude of the resulting phantom wave is given by

$$\psi = 2A \cos \pi[\Delta\tilde{\nu}x - \Delta\nu t] \sin 2\pi[\tilde{\nu}x + \nu t] \tag{5-13}$$

where we have written the equation in terms of wave numbers and frequencies and are considering finite differences. The first term gives the slowly varying amplitude of the group, and for a given value of x, in order that ψ shall return to the same value, a time interval Δt must elapse, such that the argument of the cosine term shall have decreased by 2π. Therefore

$$\pi[\Delta\tilde{\nu}x - \Delta\nu(t + \Delta t)] = \pi[\Delta\tilde{\nu}x - \Delta\nu t] - 2\pi$$

or

$$\Delta\nu \cdot \Delta t = 2 \tag{5-14}$$

Similarly, at a given time, a distance Δx must be traversed for ψ to return to the same value, such that

$$\pi[\Delta\tilde{\nu}(x + \Delta x) - \Delta\nu t] = \pi[\Delta\tilde{\nu}x - \Delta\nu t] - 2\pi$$

or

$$\Delta\tilde{\nu} \cdot \Delta x = 2 \tag{5-15}$$

From the relations, $E = h\nu$ and $p = h/\lambda = h\tilde{\nu}$, these expressions can be written

$$\Delta E \cdot \Delta t \sim h \tag{5-16}$$

and

$$\Delta p \cdot \Delta q \sim h \tag{5-17}$$

where q is a general symbol for any of the coordinates x, y, or z, associated with the corresponding momentum components p_x, p_y, or p_z. (The symbol $\sim$ indicates "is of the order of magnitude of.")

An acoustical analogy may bring out the significance of these relations. Two tuning forks of slightly different pitch produce a beat note of frequency $\Delta\nu$, and in order to measure this resultant pitch we must wait for two beats to occur. The lower the frequency, the longer the time that must be used. An infinitely short time interval can yield us no information at all about the pitch. Similarly, the wave number of the beat note (the number of waves per centimeter) cannot be measured in a distance less than one wave length. In regard to matter waves, Eqs. (5-16) and (5-17) indicate in an analogous manner that an instantaneous measurement of the exact energy of a particle is impossible, and that a precise evaluation of the momentum cannot be made in an infinitesimally small region of space. A perfect determination of one of the quantities necessitates complete ignorance of the other. These ideas are quite foreign to the classical theory of particle dynamics, wherein there is no connection between measurements of different properties of a body, and no theoretical limit to the accuracy with which such measurements can be made. The older form of the quantum theory contained the germ of these ideas, however; through the relation $E = h\nu$, the quantity E/ν, or the energy times the period of oscillation, had a certain quantized value h, and there was no significance in talking of this energy in any shorter interval of time. Also, the quantum condition for an atomic system in the form used by Bohr and Sommerfeld, $\int p\,dq = nh$, implied a fundamental unit h for the product of the coordinate and momentum, and that fractions of this unit could have no physical meaning.

This radical interpretation of the wave aspect of matter was introduced by Heisenberg[1] and further developed by Bohr,[2] with very interesting consequences. Let us consider first the application of these ideas to light quanta. It is known that the time of emission of a photon by an atomic system is of the order of 10^{-8} sec. Through Eq. (5-14) the frequency is determined in that interval to within approximately 10^8 per second. From the relation $\nu = c/\lambda$ we have that $\Delta\nu = -c\Delta\lambda/\lambda^2$, so if the light is the mercury green line with $\lambda = 5461$ Å, then

$$\Delta\nu \sim 10^8 \sim \frac{3 \times 10^{10}}{(5.5 \times 10^{-5})^2}\Delta\lambda$$

or

$$\Delta\lambda \sim 10^{-11} \text{ cm. or } 10^{-3} \text{ Å}.$$

This is of the order of magnitude of the measured fundamental width of a spectral line. Similarly, from Eq. (5-15),

$$\Delta\bar{\nu}\Delta x \sim \Delta\left(\frac{1}{\lambda}\right)\Delta x \sim \frac{1}{\lambda^2}\Delta\lambda\Delta x \sim 2$$

$$\frac{10^{-11}\Delta x}{(5.5 \times 10^{-5})^2} \sim 2$$

or

$$\Delta x \sim 600 \text{ cm}.$$

Thus a photon of this wave length cannot be localized along the axis of propagation in a region less than several meters in extent. If such a photon falls normally upon a slit-like opening, a section of which is shown in Fig. 5-1, the optical laws as embodied in the Huygens principle permit us to determine the light intensity, or the probability of observing the quantum, at some point beyond the slit. Dividing the slit opening AC hypothetically into two equal parts AD and DC, we may calculate the directions for which the light leaving the slit will have zero intensity. If to each successive point source along the line *AD* there corresponds a point source along *DC* from which the light wave, whose normal makes an angle θ with the original direction of propagation, has exactly the opposite phase, then the effects of these point sources will annul one another and the light intensity in that direction will be zero. This is true when the distance *DE* is equal to $\lambda/2$ or to any odd multiple of this quantity. Thus the smallest angle θ, at which an intensity minimum occurs, is given by

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[1] HEISENBERG, *Zeits. Physik*, **43**, 172 (1927).

[2] BOHR, *Nature*, **121**, 580 (1928).

$$\sin \theta = \frac{\lambda/2}{a/2} = \frac{\lambda}{a} \tag{5-18}$$

since θ is equal to the angle *ACE*, a being the slit width. Some light is observable at angles greater than θ, but most of it is confined within this angle. For values of the slit width large compared with λ, $\sin \theta$ is small so that there is little lateral spreading of the light beam. As the momentum of a photon is h/λ, the component of this momentum in the plane of the slit, for a photon going in the direction θ, is $p = h \sin \theta/\lambda$. Substituting for $\sin \theta$ from Eq. (5-18), we find that the product of this momentum and the slit width a is of the order h. This is in accord with the general uncertainty principle of Eq. (5-17), since a represents the accuracy with which the lateral spatial coordinate of the photon is determined.

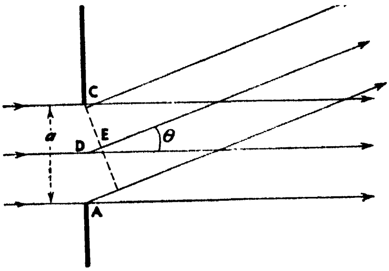

FIG. 5-1.—The diffraction of a wave at an opening.

This familiar example of light diffraction by a single slit brings out the essential point: the opening cannot be much greater than the wave length if any prominent diffraction patterns are to be observed. If this condition is not fulfilled, the angle θ is so small that the photon may be considered as obeying the laws of geometrical optics. Similar considerations apply to the case of a material particle, say an electron, and whether or not diffraction is to be expected depends on the average wave length of its component phase waves as compared with the slit size. Inasmuch as electronic speeds and energies are usually expressed in electron volts, the following relation between the accelerating potential and the associated wave length will be found convenient.

$$p = mv = \frac{h}{\lambda}$$

$$\frac{mv^2}{2} = \frac{eV}{300}$$

Hence

$$\lambda = \frac{h}{\sqrt{em}}\sqrt{\frac{150}{V}} = \frac{6.547 \times 10^{-27}}{\sqrt{4.77 \times 10^{-10} \times 9.0 \times 10^{-28}}}\sqrt{\frac{150}{V}}$$

$$\lambda = \sqrt{\frac{150}{V}}\ \text{Å} \tag{5-19}$$

to within less than 1 per cent, where the potential, V, is expressed in volts. Hence for an electron that has fallen through 150 volts, the phantom wave length is 1 Å. Assuming a slit width of 0.01 cm., such as is used in a mass spectrograph, the diffraction angle θ is given by $\theta \cong \sin\theta = \frac{\lambda}{a} = 10^{-8}/10^{-2} = 10^{-6}$ radian $= 0.2$ second of arc, which is too small to be observed. For an ion, with a mass several thousand times greater, the wave length and lateral spreading would be correspondingly even less. For such particles we therefore can determine that the lateral momentum is extremely small, at the expense of not knowing the lateral position more accurately than within the limits imposed by a rather wide slit. In the case of the usual mass spectrograph, the diffraction patterns are so small that the particles may be considered to obey the usual laws of particle dynamics, as was assumed in the previous chapters.

5-3. Analogies between Photons and Particles.—While we have treated photons and material particles by similar methods and have seen the close analogy between them, it must be pointed out that this analogy is far from complete. In the first place, material particles possess masses which to a certain extent are directly measurable, whereas the mass of a photon is a quantity derived through the relation $h\nu = mc^2$ and attributed to it in order to account for its properties when reacting with matter. As, in a sense, the mass of an electron is equally a derived quantity, this characteristic does not constitute as fundamental a difference between photons and electrons as does the reaction of the latter to electric and magnetic fields; these deflect charged material particles but apparently have no effect on the trajectory of a photon.

Electromagnetic theory predicts a definite velocity for light waves in vacuum, and for any other medium the velocity is a function of the wave length and the dispersive property of the medium. On the other hand, the phase waves associated with matter have velocities which are always greater than c, and which depend on the speed of the particle through Eq. (5-12). Further, the frequency has more physical significance for a photon than for a phase wave, although in both cases it is the wave length that is directly measured in most experiments. The group velocity for matter waves is $d\nu/d\bar{\nu}$, which is equal to the velocity of the particle, $v = p/m = h/m\lambda = h\bar{\nu}/m$. Hence $d\nu/d\bar{\nu} = h\bar{\nu}/m$ so that on integrating, $\nu = (h\bar{\nu}^2/2m) + K$. Thus the phase waves' frequency is undetermined to the extent of an additive constant. This is usually taken as zero, since on differentiating to obtain the group velocity (the only quantity ever observed) the constant disappears. For a photon, the velocity in a vacuum, c, is known very accurately, and, therefore, with an experimental measure of λ, the frequency is determined through the relation $\lambda\nu = c$. For very long electromagnetic waves, such as those used in radio, ν is directly measurable in terms of frequency standards which in turn may be compared with clocks.

The electric and magnetic vectors of a light wave are also quantities measurable by means of ordinary apparatus and are particularly familiar to us in the limit of static electric and magnetic fields. In this sense they have a reality not shared by the complex scalar quantity ψ, the periodic variation of which is associated with a particle of matter. Upon the quantum theory, ψ is essentially unobservable; only the square of its absolute magnitude has any physical meaning, *i.e.*, the probability of observing a particle at a specified point. This interpretation is closely analogous, however, to that applied to the electromagnetic waves, wherein the square of the electric or magnetic vector, which represents the energy flux or intensity, is interpreted as the probability of observing a photon in that region.

Material particles, such as electrons and atoms, exhibit an axial polarity inasmuch as certain mechanical and magnetic moments are associated with them, as will be discussed more fully in Chap VII. There is also a certain preferred direction, such as that of the electric or magnetic vector, in the case of a plane-polarized electromagnetic wave. For a circularly polarized wave there is an associated angular momentum. Since a plane-polarized wave may be considered as the sum of two circularly polarized disturbances, we can see that the polarity of optical phenomena would be capable of explanation on the assumption of an angular momentum associated with a photon, so that it too can exhibit a preferred direction, as can a particle of matter. This angular momentum vector may be shown to be directed along the axis of propagation of the photon, whereas in the case of one electron in an atom we shall see that the angular momentum vector is perpendicular to what is generally considered the direction of motion of the electron. For more massive particles, such as atoms, the magnetic and mechanical moments appear not to be conditioned by the particle's trajectory, but by the external fields, as in the Stern-Gerlach experiment (Chap. VII).

For a more complete account of the uncertainty principle and its implications, and a discussion of the many theoretical problems connected with the motion and interaction of photons and particles, the reader is referred to the treatises and articles on quantum mechanics by Heisenberg,[1]

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[1] HEISENBERG, *Zeits. Physik*, **43**, 172 (1927).

HEISENBERG, "The Physical Principles of the Quantum Theory," University Chicago Press (1930).

Darwin,[1] Landé,[2] Mott,[3] Frenkel,[4] and Dirac.[5] A very lucid account of the reconciliation between the wave and particle theories has been given by Darrow.[6]

5-4. Diffraction by Gratings and Lattices.—As we have seen in the previous sections, the wave lengths of the matter waves associated with electrons and with atoms are in general so short that it would be very difficult to detect diffraction effects from openings or gratings which can be constructed mechanically. Though these effects have been observed with ruled gratings, as will be mentioned later, the most convenient instrument for detecting diffraction of matter waves is the regular space grouping of the atoms or ions provided by a crystal. The study of crystallography together with the investigation of crystal structure by means of X-rays has given us a very clear and complete picture of a perfect crystal as a highly regular spatial lattice of atoms or ions. The forces holding these units in position are still not completely understood, but the particular spatial characteristics of crystal lattices, which fall into a finite number of types, have been very thoroughly investigated. The information gained by the diffraction of X-rays from crystals, the wave length having been measured previously with a ruled grating, has afforded very convincing confirmation of the validity of this fundamental conception of crystal structure. These X-ray investigations will be deferred to a later chapter and we shall now make use of the knowledge obtained in this way in order to examine the diffraction of matter waves.

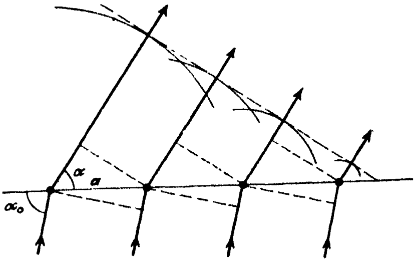

FIG. 5-2.—Diffraction from a one-dimensional grating.

5-5. One-dimensional Grating. We shall first consider the effects to be expected from a one-dimensional lattice or ordinary plane ruled grating on the simple form of the Huygens principle. The points of Fig. 5-2 represent the intersections of the open spaces of a ruled grating with a plane normal to the rulings. These points are the centers of the emerging wave disturbances in the plane of the paper. If a plane wave (advancing in the plane of the paper), whose normal lies along the direction defined by the angle α_0, falls on the grating, we have elementary wavelets emerging from the series of points, the various envelopes of these waves forming the wave fronts of the diffracted beams. If the grating openings reflect to some extent, a similar scheme of waves is formed on the incidence side. Due to the angle of incidence α_0, each successive system of wavelets from left to right lags in phase behind the preceding one, because the original plane wave reaches the openings at different times. A further phase retardation occurs for the emerging wavelets, depending on the angle of diffraction. Constructive interference among the waves from the several openings gives rise to intense diffracted beams for those directions in which the sum of the phase retardations is an integral multiple of 2π, *i.e.*, for those directions in which the path difference between adjacent beams is an integral multiple of a wave length. From the geometry of the figure we see that this condition is fulfilled when

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[1] DARWIN, *Proc. Roy. Soc.*, **117**, 258 (1927); **130**, 632 (1931); *Science*, **73**, 653 (1931).

[2] LANDÉ, "Vorlesungen über Wellenmechanik," Akad. Verlag. Gesell., Leipzig (1930).

[3] MOTT, "An Outline of Wave Mechanics," Cambridge University Press (1930).

[4] FRENKEL, "Einführung in die Wellenmechanik," Springer (1929).

[5] DIRAC, "Principles of Quantum Mechanics," Oxford University Press (1930).

[6] DARROW, *Bell System Technical J.*, **9**, 163 (1930).

$$a(\cos \alpha - \cos \alpha_0) = H\lambda \tag{5-20}$$

where a is the grating constant, or distance between corresponding points in adjacent openings, α is the observed angle of the diffraction maximum, and H is an integer. (The signs of the cosines must be interchanged if α_0 is less than α.) Considering normal incidence ($\alpha_0 = 90°$) and writing θ for $90° - \alpha$, we obtain the familiar equation

$$a \sin \theta = H\lambda \tag{5-21}$$

From a knowledge of a, H, and the angles, the wave length can be computed. (When used with X-rays or electrons, the original beam is made so narrow that only a small portion of the grating is used and the diffracted beams from adjacent openings are consequently practically coincident; no lens is required to bring them to a sharp focus, as is needed with light, when a large portion of the grating surface is used.)

The use of such ruled gratings for which a is of the order of 10^{-4} cm. has long been familiar in the field of optics. As has already been mentioned, their use has been extended to the short wave-length region of X-rays and has thus provided wave-length measurements independent of any crystal-structure hypothesis. An attempt was made by Knauer and Stern[1] to employ a grating to establish the wave nature of such large material particles as entire atomic systems, but the effort was not very successful since only an indication of the first diffraction maximum was obtained. The velocity distribution of a stream of atoms is rather wide, so that the associated wave length is not well defined.

The wave length of the phantom waves associated with a stream of electrons of nearly uniform velocity has, however, been successfully measured by Rupp.[2] The method is similar to that used with X-rays and is indicated in Fig. 5-3. A narrow beam of electrons strikes the grating at a small glancing angle α_0; the specularly reflected beam [$H = 0$ in Eq. (5-20)] also makes an angle α_0 with the grating, while the first diffracted beam occurs at an angle $\alpha_0 + \alpha'$ with the grating. Equation (5-20) may be written

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[1] Knauer and Stern, *Zeits. Physik*, **53**, 779 (1929).

[2] Rupp, *Zeits. Physik*, **52**, 8 (1929).

$$a[\cos \alpha_0 - \cos (\alpha_0 + \alpha')] = H\lambda$$
$$a[\cos \alpha_0 - \cos \alpha_0 \cos \alpha' + \sin \alpha_0 \sin \alpha'] = H\lambda$$

or, as the angles are small, we may set $\cos \alpha_0 = 1 - \frac{\alpha_0^2}{2}$ and $\cos \alpha' = 1 - \frac{\alpha'^2}{2}$, and dropping a term in $\alpha_0^2\alpha'^2$, we obtain

$$H\lambda = \frac{a}{2}\alpha'(\alpha' + 2\alpha_0) \qquad (5\text{-}22)$$

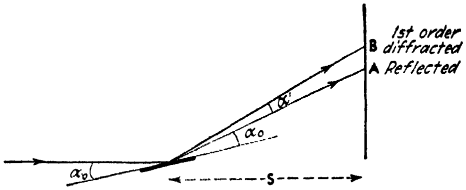

FIG. 5-3.—The method of using a plane grating to measure the effective wave length of an electron beam. The angles are shown considerably exaggerated.

This equation indicates the advantage of using almost tangential incidence; as α_0 becomes smaller, α' increases, so that the faint diffracted beam is moved farther from the strong regularly reflected one and observation is facilitated. The directly measured quantities are S, the distance from grating to photographic plate, and the separation AB of the images on the plate of the reflected and diffracted beams. As the angles are all very small, α' may be taken as equal to AB/S. The angle α_0 is difficult to measure directly, but it may be calculated if a second-order diffracted ray is also observed; we then have two equations similar to Eq. (5-22) from which to determine λ and α_0, with H equal to 1 and 2, for the two cases, respectively. The grating constant a may be determined through the use of the grating in an optical spectrometer and the observation of the angle of diffraction of some known wave length of light. The wave length of the electrons measured in this way by Rupp agreed within a few per cent with that determined from the applied potential by Eq. (5-19). This obviously constitutes a very striking confirmation of the wave nature of an electron.

5-6. Two-dimensional Grating or Surface Lattice.—The two-dimensional lattice or grating provided by a crystal surface may also be used to measure wave length. The general type of phenomena to be observed is familiar from the use of two crossed line gratings with visible light. The points of Fig. 5-4 represent the resulting openings of two crossed gratings whose lines make an angle ϕ with one another, or they may represent the atomic lattice points which act as the centers of oscillation producing the scattered wavelets. (The lattice lies in the plane of the paper; waves enter from above and are diffracted either into the paper or back up again.) The distances between neighboring atoms along the two crystal axes are given by a and b. The condition that the wavelets leaving the points P and Q at an angle α to one axis should have the same phase is given, as before, by the relation

$$a(\cos \alpha - \cos \alpha_0) = H\lambda \tag{5-23}$$

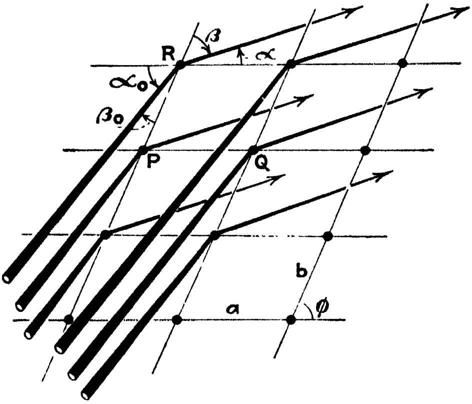

FIG. 5-4.—A surface lattice or two crossed line gratings.

Similarly, the condition that the waves leaving P and R at an angle β with the other axis of the crystal should be in phase is

$$b(\cos \beta - \cos \beta_0) = K\lambda \tag{5-24}$$

where H and K are integers. If both these equations are satisfied a strong maximum is observed. As α and β are independent of one another, it is always possible to satisfy these two relations for any value of λ; *i.e.*, a spectrum is formed for all wave lengths, as is the case with a one-dimensional lattice or plane grating. For simplicity, let us consider the case of normal incidence, *i.e.*, $\cos \alpha_0 = \cos \beta_0 = 0$. The equations are then

$$\cos \alpha = \frac{H}{a}\lambda \qquad \cos \beta = \frac{K}{b}\lambda \tag{5-25}$$

The interference maxima are distributed on a photographic plate parallel to the plane of the grating and distance S from it, in the manner shown in Fig. 5-5, for a given value of λ. The two indices associated with each maximum indicate the order of the two spectra formed by the crossed gratings. Thus the spot $-2\ 1$ indicates that $H = -2$ and $K = 1$; the direct beam is given by 0 0. A distance such as $0\,0 \rightarrow -1\,0$ is equal to $S \cot \alpha$, which for α near 90° is approximately equal to $S \cos \alpha$ or $S\lambda/a$. Thus the distance between neighboring spots with a common second index is inversely proportional to a, and similarly the distance between spots with a common first index is inversely proportional to b. The angle between coordinate lines on the plate is evidently the same as that between the two axes of the crystal lattice.

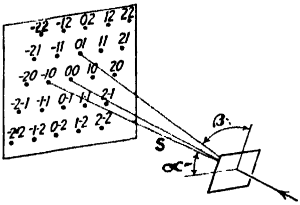

FIG. 5-5.—The diffraction pattern produced by a surface lattice.

Since a stream of atoms impinging on a crystal face does not effectively penetrate far into it, the surface layer of atoms acts as a reflecting two-dimensional grating for the phase waves associated with the atoms. The experiment of directing a stream of atoms at a crystal face and observing the number of them reflected at various angles has been performed by Stern[1] and his collaborators and by Johnson.[2] The technique of producing and detecting the atom beam is very difficult, but well-defined diffraction patterns have been observed. By reason of the Maxwellian distribution of velocities in the atomic stream, the wavelength range is rather large, but within the error due to this factor the experimental results are in excellent agreement with the theory of the wave nature of atoms. A complete discussion of these interesting experiments is to be found in the original papers or in the treatise on molecular rays by Fraser.[3]

Diffraction from a two-dimensional grating of this kind has also been observed with electrons. Here again the experiments are fully in accord with the wave theory. A complete account of this work may be found in an article by Kikuchi[4] and in the book of G. P. Thomson.[5] The patterns found with mica [$KH_2Al_3(SiO_4)_3$] by Kikuchi, which may also be obtained with the apparatus to be described later, are particularly striking. A homogeneous beam of electrons falls normally upon a very thin sheet of mica, in the manner indicated in Fig. 5-5. The lattice points on the surface of a cleavage plane are arranged approximately in an array for which $a = b = 5.17 \times 10^{-8}$ cm. with $\phi = 60°$. In consequence of this, the spots observed on the photographic plate are arranged symmetrically at the corners of closely packed equilateral triangles, as in Fig. 5-6, the distance between spots on a plate S cm. from the mica being given by $S\lambda/a$, as in the previous discussion. From this the wave length can be calculated and compared with that deduced from the voltage through which the electrons have fallen. We are enabled to neglect the effect of successive planes parallel to the cleavage surface, if the mica is very thin. For a film of the order of 10^{-6} cm. thick, which yields good patterns of this type, there are only about 20 planes, so their interaction may be neglected. To interpret the results obtained with considerably thicker films, we should have to take into account the effect of a three-dimensional lattice.

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[1] STERN, *Naturwiss.*, **17**, 391 (1929).
ESTERMANN and STERN, *Zeits. Physik*, **61**, 95 (1930).

[2] JOHNSON, *Phys. Rev.*, **35**, 1299 (1930); *J. Franklin Inst.*, **210**, 135 (1930).

[3] FRASER, "Molecular Rays," Cambridge University Press (1931).

[4] KIKUCHI, *Physik. Zeits.*, **31**, 777 (1930).

[5] THOMSON, G. P., "The Wave Mechanics of Free Electrons," McGraw-Hill (1930).

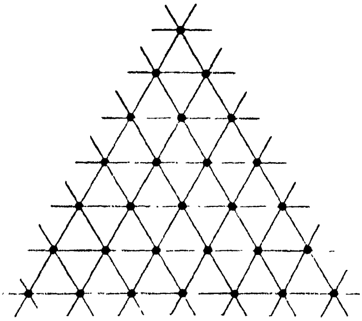


FIG. 5-6.—The type of diffraction pattern obtained from a two-dimensional lattice of thin mica.

5-7. Three-dimensional Grating or Space Lattice.—The use of a crystal space lattice or three-dimensional grating has given the most complete information with regard to the wave length of both X-ray photons and material particles. A typical example of a simple space lattice is shown in Fig. 5-7. This indicates a sample block containing eight elementary cells, the crystal axes making angles ξ, η, and ζ with one another. Let us consider that there is incident on the crystal a plane wave whose normal makes angles α_0, β_0, and γ_0 with these axes. The conditions that wavelets leaving the points P, Q, and R should be in phase along a direction defined by the angles α and β are evidently given by Eqs. (5-23) and (5-24). In addition there is now the necessity that wavelets from P and S should be also in phase, which requires a third condition of the same form. The important point in connection with these three equations is that they no longer define a direction of con-

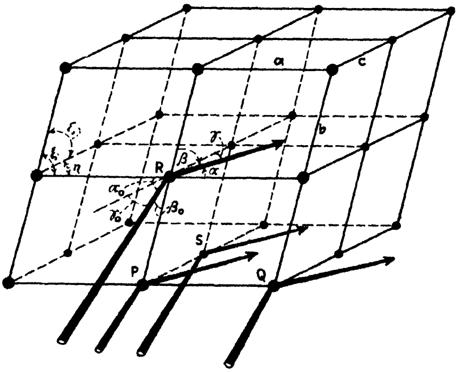


FIG. 5-7.—A three-dimensional grating or space lattice. Eight elementary cells are shown with an atom at each corner.

structive interference for any arbitrary value of λ, for the angles are not all independent. Only for particular wave lengths can a diffraction pattern be formed.

For simplicity in dealing with these additional restrictions, let us limit our considerations to those common crystals in which the axes are all mutually perpendicular. The cosines of the angles defining the incident and diffracted beams are then the direction cosines referred to axes taken along the crystal axes. The condition of interdependence between the angles that was mentioned above is then that the sums of the squares of the direction cosines must equal unity, as is a well-known proposition of solid analytical geometry. We thus have the following five equations, with seven variables—the six direction cosines and the wave length:

$$a(\cos\alpha - \cos\alpha_0) = H\lambda \tag{5-26}$$
$$b(\cos\beta - \cos\beta_0) = K\lambda \tag{5-27}$$
$$c(\cos\gamma - \cos\gamma_0) = L\lambda \tag{5-28}$$
$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1 \tag{5-29}$$
$$\cos^2\alpha_0 + \cos^2\beta_0 + \cos^2\gamma_0 = 1 \tag{5-30}$$

The different methods of using a spatial lattice, as will be described in this chapter and in that on X-rays, depend upon the choice as to which quantities are to be varied and which left fixed. In order to obtain an expression for the wave lengths for which diffraction maxima do occur, let us divide each of the first three of these equations by its respective grating constant, a, b, c, square the resulting equations and add them together. Substituting Eqs. (5-29) and (5-30) into the result gives us

$$2 - 2[\cos\alpha\cos\alpha_0 + \cos\beta\cos\beta_0 + \cos\gamma\cos\gamma_0] = \left(\frac{H^2}{a^2} + \frac{K^2}{b^2} + \frac{L^2}{c^2}\right)\lambda^2 \tag{5-31}$$

The bracket on the left is the cosine of the angle between the incident and diffracted beams; *i.e.*, it is the cosine of the angle of deflection ψ, measured from the continuation of the direction of incidence. Hence

$$2(1 - \cos\psi) = \left(\frac{H^2}{a^2} + \frac{K^2}{b^2} + \frac{L^2}{c^2}\right)\lambda^2 \tag{5-32}$$

Or since $1 - \cos\psi = 2\sin^2\frac{\psi}{2}$, and if we let $\theta = \frac{\psi}{2}$,

$$2\sin\theta = \sqrt{\frac{H^2}{a^2} + \frac{K^2}{b^2} + \frac{L^2}{c^2}}\,\lambda \tag{5-33}$$

For a cubic lattice, for which $a = b = c$, this becomes

$$2\,a\sin\theta = \sqrt{H^2 + K^2 + L^2}\,\lambda \tag{5-34}$$

An alternative and simpler conception of this process of diffraction by a space lattice is due to Bragg. For a beam deviated through an angle $\psi = 2\theta$ in accordance with Eq. (5-33) or (5-34), it is always possible to find a series of parallel planes containing all the atoms of the crystal, such that the incident ray is apparently specularly reflected from these planes as if from a pile of mirrors, the incident and reflected glancing angles being each equal to θ. These Bragg "reflection" planes are not necessarily the natural cleavage planes of the crystal, although they may be. From Fig. 5-8 it is evident that the path difference for rays specularly reflected by successive planes through an angle $\psi = 2\theta$ is equal to $2d \sin \theta$, where d is the perpendicular distance between the planes. If this path difference is an integral multiple of a wave length, we have reinforcement for this wave length in this direction; hence, the condition for a diffraction maximum may be concisely stated by the familiar Bragg relation

$$2d \sin \theta = n\lambda \tag{5-35}$$

where n is an integer. We may find the relation between d, the index numbers H, K, L and the grating constants a, b, c, by comparing this with Eq. (5-33). This shows that

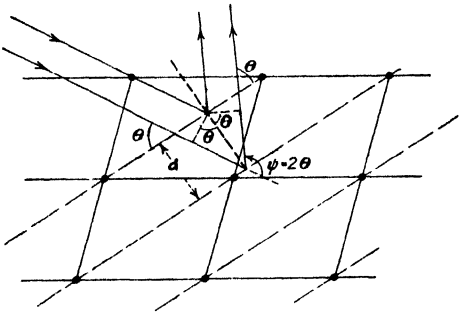


FIG. 5-8.—Diffraction in a crystal may be considered as specular reflection from parallel planes passing through the atoms.

$$d = \frac{n}{\sqrt{\dfrac{H^2}{a^2} + \dfrac{K^2}{b^2} + \dfrac{L^2}{c^2}}} \tag{5-36}$$

If we define the integers h, k, l, by setting

$$nh = H, \quad nk = K, \quad nl = L \tag{5-37}$$

where n is the greatest common divisor of H, K, L, we have

$$d = \frac{1}{\sqrt{\dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{l^2}{c^2}}} \tag{5-38}$$

For the cubic-type lattice, where $a = b = c$, this becomes

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{5-39}$$

We have defined d as the perpendicular distance between the Bragg reflection planes. We shall now show that the letters h, k, l are the so-called *Miller indices* which designate the orientation of the reflection planes with respect to the crystal axes. If the origin of coordinates is chosen to lie in one of the Bragg planes, the intercepts of the next parallel plane of this family along the axes are, say, ua, vb, wc, where u, v, w are fractions of the form $1/q$, q being an integer and a, b, c the lengths of the three edges of the crystal unit cell. The equation of this plane is then

$$\frac{x}{ua} + \frac{y}{vb} + \frac{z}{wc} = 1$$

and its perpendicular distance from the origin, and hence the perpendicular distance between the planes of this family, is, by a theorem of coordinate geometry,

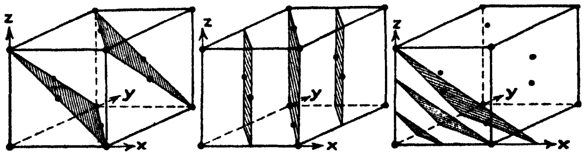
$$d = \frac{1}{\sqrt{\dfrac{1}{u^2a^2} + \dfrac{1}{v^2b^2} + \dfrac{1}{w^2c^2}}}$$

We now write $h = 1/u$, $k = 1/v$, $l = 1/w$, so that h, k, l are the reciprocals of the fractions of unit distances contained in each intercept; by definition, the Miller indices. Then

$$d = \frac{1}{\sqrt{\dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{l^2}{c^2}}}$$

This is the same as Eq. (5-38), indicating that the h, k, l, appearing there, are the Miller indices.

In addition to simple cubic lattices, there are two other common types of cubic crystals: the face-centered lattice, in which atoms are found at the centers of the six faces of the unit cell as well as at the eight corners, as in Al, Cu, Ag, Pt; and the body-centered type, in which there is an atom at the center of the unit block in addition to those at the corners, examples being Na, K, Mo, W. For simplicity in discussing the diffraction patterns obtained from such crystals, we may observe from Eq. (5-37) that any order, n, of Bragg reflection from planes with Miller indices (hkl) can be considered as the first-order Bragg reflection from planes designated by $[HKL]$. Planes defined by these latter numbers are parallel to the corresponding (hkl) planes, but the distance between them is equal to the distance between the (hkl) planes divided by the order number n; the $[HKL]$ planes therefore include the parallel (hkl) planes as well as the intermediate ones. For simple cubic lattices, all atomic planes specified by $[HKL]$ contain all the atoms in the crystal and hence are Bragg reflection planes; this is not true, in general, for face- and body-centered systems. Inspection of Fig. 5-9 indicates that all atoms in a face-centered lattice are not included in a parallel set of planes for arbitrary values of H, K, and L. Thus for a plane $[HKL]$ the intersection with say the xy face passes through the atom at the center of this face if H and K are both even or both odd, and its intersection with the xz face passes through that center atom if H and L are both even or both odd; hence the planes include all the atoms and reflect as Bragg planes only if H and K and L are all even or all odd. Thus some of the beams that are diffracted from a simple cubic crystal will be absent from the spectrum due to a face-centered cubic lattice. A similar consideration applies to the body-centered type, for which an analogous argument shows that only those beams will be present for which $H + K + L = 2m$, where m is an integer. The diffracted beams from the usual cubic crystals are therefore given by Eq. (5-34) limited by the following conditions:



[111] [220] [243]

FIG. 5-9.—Atomic planes in face-centered crystals. In the center figure the middle plane would be called [110] if the two other planes were not present (as would be the case if the crystal were simple cubic). In the two right-hand figures, some of the planes are determined by atoms in adjacent cubes. It is evident that atoms exist halfway between the [243] planes, annulling the waves reflected from these planes.

Simple cubic.	$H, K, L,$	arbitrary
Face-centered cubic.	$H, K, L,$	all even or all odd
Body-centered cubic.	$H + K + L,$	even

For a further discussion of crystal structure and, in particular, the diffraction of X-rays by crystals, reference should be made to the treatises of Wyckoff[1] or Schleede and Schneider.[2]

Three-dimensional crystal lattices have been used to measure the wave length of X-rays and also that of the phantom waves associated with matter. In view of the necessary distance of penetration into the crystal before the spatial characteristics become effective, this type of experiment is difficult to perform for a beam of atoms whose dimensions are of the order of magnitude of those in the crystal. It has, however, been accomplished by Dempster[3] and more recently by Sugiura.[4] The latter obtained a beam of protons by ionizing the hydrogen which diffused into the apparatus through a hot palladium tube. The protons were accelerated and the beam rendered homogeneous in velocity by deflection in a magnetic field. The stream then fell on a thin film of platinum or tungsten, and the directions of the reflected beams were observed with an exploring electrode and electrometer. The wave lengths as computed from the observed values of sin θ, by means of Eq. (5-33), agreed to within a few per cent with those calculated from the relation $\lambda = h/Mv$, where M is the mass of a proton. The protons used had fallen through 300 volts and so had a wave length of 0.0164 Å.

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[1] WYCKOFF, "The Structure of Crystals," Chemical Catalog Company (1931).

[2] SCHLEEDE and SCHNEIDER, "Röntgenspektroskopie," deGruyter (1929).

[3] DEMPSTER, *Phys. Rev.*, **35**, 298, 1405 (1930).

[4] SUGIURA, *Sci. Papers Inst. Phys. and Chem. Res., Tokyo*, **16**, 29 (1931).

The original work on electrons, performed by Davisson and Germer and by Thomson, to which reference has already been made, was done with these space lattices. Davisson and Germer reflected electrons from a nickel crystal and detected the diffracted beams electrically. Thomson directed an electron beam on to thin crystalline films and observed the transmitted diffraction patterns photographically. The results of these experiments provide a very beautiful verification of the validity of the wave concept of electrons. The measured values of λ and those calculated from the applied potential by means of Eq. (5-19) are in excellent agreement over a very wide range.

Evidence from this work on electron diffraction has been found for an index of refraction of electron waves in crystals. That is, owing to the effective potential wall at the surface of the crystal, the electrons acquire greater energy on penetrating it. Thus their wave length is shortened, which is equivalent to an index of refraction greater than unity, just as is the case with light waves entering glass. The normal of the electron wave is bent toward the inward normal of the crystal surface. The potential barrier at the crystal surface is found from these experiments to be of the order of 10 to 20 volts; its significance will be further discussed in the subsequent chapter.

A complete account of this work on electron diffraction is to be found in the article by Rupp[1] or in the books by Thomson[2] and by Mark and Wierl.[3]

5-8. Scattering of α Particles and Positive Ions by Atomic Systems.—The elementary particles of greatest energy which have been available for physical experiments are the α particles emitted by radioactive substances. These, on account of their great velocities, have very short wave lengths and so should obey the classical equations of motion of a particle, even when passing through atomic systems, to a very close approximation. Thus if we know the law of force existing around an atomic system, we can apply the equations of motion of a particle in such a field in order to calculate the angle through which a particle, of a given energy and proceeding in a given direction, will be deflected. This problem of α-particle scattering by individual atomic systems was first studied by Rutherford.[1] On the assumption of an inverse-square-force field, *i.e.*, the Coulomb field surrounding a point charge Ze with infinite mass, the fraction of the α particles scattered per unit solid angle in a direction making an angle θ with the original beam, by an atomic nucleus, is given by

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[1] RUPP, *Ergeb. Exakt. Naturwiss.*, **9**, 79 (1930).

[2] THOMSON, G. P., "The Wave Mechanics of Free Electrons," McGraw-Hill (1930).

[3] MARK and WIERL, "Die Experimentalen und Theoretischen Grundlagen der Elektronenbeugung," Bornträger (1931).

$$y = \left[\frac{e^2Z}{MV^2}\operatorname{cosec}^2\frac{\theta}{2}\right]^2 \tag{5-40}$$

where e is the elementary charge, and M and V the mass and velocity of the α particle. This relation was tested experimentally by Rutherford, and its verification was evidence for the validity of the assumptions involved. As such it was of the greatest importance in the early development of atomic physics, for it supplied direct evidence for the nuclear type of atom. An α particle possesses so much energy that it penetrates the outer electron structure assumed to surround the nucleus and is deflected only by this central body possessing a charge Ze equal to that of the enveloping electrons. From α-particle scattering measurements Z may be calculated, and this evidence provides an important check on the theory of atomic structure determined from optical and X-ray data. Likewise from these scattering experiments an estimate can be made of the least distance from the nucleus at which the inverse square law is valid. This provides an upper limit to the nuclear dimensions, which is found to be of the order of from 10^{-13} to 10^{-12} cm. As atomic radii are of the order of 10^{-8} cm., these distances are less than a ten-thousandth of the effective atomic radius. Thus the great majority of the mass of an atom occupies a volume of about 10^{-12} of the volume occupied by the atom as a whole.

In the case of slow enough positive ions, however, we should expect phenomena to appear which would be more difficult to interpret, for as the phantom wave length becomes longer the complicated diffraction effects would be expected to become evident. Very interesting experiments on the effective cross section of atoms for collisions with positive ions, and the interception and scattering of these ions by various gases, have been performed by a number of investigators.[2] Our knowledge of the external structure of atoms and the resultant effect of this on positive-ion interception is, however, insufficient to enable an accurate comparison to be made of these experimental results with atomic theory.

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[1] Rutherford, *Phil. Mag.*, **11**, 166 (1906); **21**, 669 (1911).

[2] Dempster, *Phil. Mag.*, **3**, 115 (1927).
Thomson, G. P., *Phil. Mag.*, **1**, 961 (1926); **2**, 1076 (1926).
Ramsauer and Beeck, *Ann. Physik*, **87**, 1 (1928).
Kallman and Rosen, *Zeits. Physik*, **61**, 61, 332 (1930); **64**, 806 (1930).

However, many interesting phenomena do emerge from these researches. For certain critical velocities of the positive ions, the effective cross sections of the gas molecules reach a maximum value; *i.e.*, for either slower or faster ions, fewer deflecting collisions occur over the same distance and at the same pressure. This indicates a resonance effect which might qualitatively have been expected on a wave theory of the ions. Furthermore, when the ions are those of the gas through which they are moving, the resonance effects become particularly pronounced. One of the most striking examples of this is the scattering of α particles (which are doubly charged helium atoms) by helium. The wave mechanical calculations for this case have been performed by Mott,[1] and by Taylor[2] and the resulting predictions, which differ markedly from those of classical dynamics, have been experimentally verified by Chadwick,[3] by Blackett and Champion,[4] and by Wright.[5]

5-9. Experiment on Electron Diffraction.—The simplest method of observing the phenomenon of electron diffraction is by the transmission of electrons through thin metallic films composed of crystal aggregates oriented more or less at random. This method was first suggested by Thomson[6] and, with simple apparatus, it yields very striking diffraction effects. A random orientation of the crystal blocks in the film is characteristic of gold films whether sputtered or otherwise prepared. The films of most other metals, such as aluminium, nickel, or copper, apparently have more or less preferred directions of orientation, resulting in diffraction patterns composed of spots or arcs instead of the symmetrical circular designs formed by gold.

The diffraction pattern to be expected on the basis of Eq. (5-33) or (5-34) from a random distribution of crystals in a thin film is indicated in Fig. 5-10. For an electron beam of a definite velocity, and hence with a definite wave length, and with any given choice of the indices H, K, L, a diffracted beam will appear making some angle $2\theta_1$ with the original direction. On the Bragg conception of specularly reflecting planes this corresponds to the existence of a crystal block so oriented that the normal to the plane $[HKL]$ lies in the plane of the incident and reflected rays, the angles that these two beams make with this reflecting plane being each equal to θ_1. Constructive interference between the beams reflected from the layers of similar parallel planes within the crystal results in a blackening of the photographic plate at the point B. For a random distribution of crystal blocks in the film, we shall have a random orientation in azimuth around the incident beam of the normals of similar planes in different crystals, resulting in a uniform azimuthal distribution of such spots, thus forming a circular ring on the plate. For the same wave length and grating constant but for a different choice of $[HKL]$, reflection from a properly oriented crystal occurs at some other angle θ_2, the random orientation in azimuth of other similar crystals resulting in a second ring of radius AC.

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[1] MOTT, *Proc. Roy. Soc.*, **126**, 259 (1930).

[2] TAYLOR, *Proc. Roy. Soc.*, **136**, 605 (1932).

[3] CHADWICK, *Proc. Roy. Soc.*, **128**, 114 (1930).

[4] BLACKETT and CHAMPION, *Proc. Roy. Soc.*, **130**, 380 (1931).

[5] WRIGHT, *Proc. Roy. Soc.*, **137**, 677 (1932).

[6] THOMSON, G. P., *Proc. Roy. Soc.*, **117**, 600 (1928); **119**, 651 (1928).

The radii of the different rings corresponding to different combinations of H, K, L are related to their respective angles of deviation by the

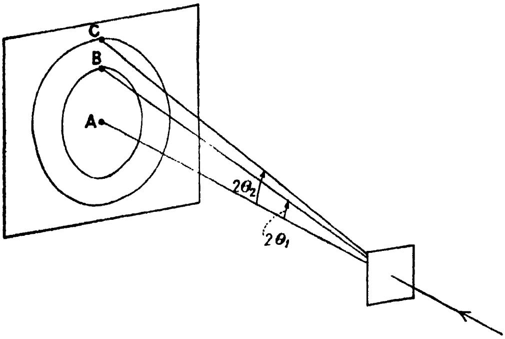

FIG. 5-10.—Formation of circular diffraction patterns due to the random orientation of the crystals in a thin film.

equation $\tan 2\theta = r/S$, where S is the distance from the scattering film to the photographic plate. For values of 2θ up to about 8°, an error of less than 1 per cent is made in replacing the sine or tangent of the angle by the angle itself, in radian measure. Since the diffraction angles are almost always less than this amount, we may write

$$2\theta = \frac{r}{S}$$

and Eq. (5-34) becomes

$$\lambda\sqrt{H^2 + K^2 + L^2} = 2a \sin \theta = 2a\theta = \frac{ar}{S}$$

Hence

$$\lambda = \frac{ar}{S} \frac{1}{\sqrt{H^2 + K^2 + L^2}} \tag{5-41}$$

This gives the wave length of the phantom waves associated with the electrons as a function of the grating constant, a, of the crystal, the distance, S, and the different radii of the rings caused by various combinations of the indices H, K, L. If the crystal is face- or body-centered, the indices are subject to the conditions previously mentioned. Gold crystals are known from X-ray measurements to be face-centered, so that with a gold film we should obtain rings corresponding to values of H, K, L, which are all even or all odd. For a body-centered molybdenum film, the sum of the indices must be even, while for a simple cubic crystal, such as sodium chloride, there are no restrictions. For these three types, rings due to the following combinations should occur.

Simple cubic				Body-centered cubic				Face-centered cubic			
H	K	L	$\sqrt{H^2+K^2+L^2}$	H	K	L	$\sqrt{H^2+K^2+L^2}$	H	K	L	$\sqrt{H^2+K^2+L^2}$
0	0	1	1								
0	1	1	$\sqrt{2}$	0	1	1	$\sqrt{2}$				
1	1	1	$\sqrt{3}$					1	1	1	$\sqrt{3}$
0	0	2	2	0	0	2	2	0	0	2	2
0	1	2	$\sqrt{5}$								
1	1	2	$\sqrt{6}$	1	1	2	$\sqrt{6}$				
0	2	2	$\sqrt{8}$	0	2	2	$\sqrt{8}$	0	2	2	$\sqrt{8}$
1	2	2	3								
0	0	3	3								
Etc.											

The values of the quantity $\sqrt{H^2 + K^2 + L^2}$ are, for a given wave length, directly proportional to the radii of the rings; it may happen that the rings predicted by two permissible values of the indices lie so close together that they cannot be seen separately. For instance, the circles due to [113] and [222] may be unresolved, since the square roots of the sums of the squares of these indices are $\sqrt{11}$ and $\sqrt{12}$ or 3.32 and 3.46, respectively. As the number of atoms in these planes is not the same, and as the planes themselves vary in the frequency with which they occur, the intensities of the rings are not the same and a weighing factor should be included if extreme accuracy is desired when computing the wave length from a set of unresolved rings. With only moderately accurate measuring facilities, this refinement may be omitted without introducing any great error.

In the use of the diffraction apparatus to be described, the verification of the wave theory of electrons consists in an agreement between the observed ring patterns obtained from electrons of given energy and those calculated as above, using allowed values of the indices, and in the agreement of the wave length deduced from Eq. (5-41) with that calculated from the known accelerating potential by the use of Eq. (5-19). The ring diameters and the distance S are measured directly; the grating constant a may either be assumed to be known from X-ray data or it may be calculated from a knowledge of the lattice type, the density, the atomic weight, and Avogadro's number.

The calculation of the grating constant is very simple if we may assume that the measured values of the density from large masses of the substance are a close approximation to that of a single crystal. In general this assumption yields the correct result if we use the greatest value of the density as determined from samples of the material which have been subjected to different treatments, *i.e.*, cast, wrought, vacuum distilled, etc. Considering Fig. 5-7, we see that each of the atoms at the corners of a unit cell of a simple cubic lattice is shared by eight neighboring cells. Hence only one-eighth of each of these eight atoms effectively belongs to one cell, thus giving us one atom per cell, for the simple cubic type. For a face-centered lattice, however, there are six more atoms each shared by two adjacent cells; one-half of these six, therefore, belong to one cell, giving us as the total complement per face-centered cell, $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$. For a body-centered system the central atom is shared by no other cell, so that the number of atoms per cell is $8 \times \frac{1}{8} + 1 = 2$. If we multiply this number n of atoms associated with a unit cell by the mass of each atom, which is given by M/N, M being the atomic weight and N being Avogadro's number (the number of atoms per gram-atom), we obtain the mass of a unit cell. This mass is also given by the volume of the unit cell, namely a^3, multiplied by the density ρ. Equating these two expressions for the mass, we have

$$n\frac{M}{N} = a^3\rho$$

or

$$a = \left(\frac{nM}{N\rho}\right)^{\frac{1}{3}} \tag{5-42}$$

where $n = 1$, for simple cubic.
$n = 2$, for body-centered cubic.
$n = 4$, for face-centered cubic.

Taking gold as an example, we have $n = 4$, $M = 197.2$, $\rho = 19.33$, with $N = 6.06 \times 10^{23}$, yielding $a = 4.067 \times 10^{-8}$ cm. The most probable value of a from X-ray diffraction data is 4.064×10^{-8} cm.

Various simple designs of electron-diffraction apparatus suitable for class-room demonstration and elementary experimental work have been described by Kirchner,[1] Rupp,[2] Lebedeff,[3] and Phillips.[4] The method employed by Lebedeff probably yields diffraction patterns of the greatest intensity, but it involves the added complication of a magnetic focusing field and a slight loss in sharpness of definition. An apparatus that has

[1] Kirchner, *Physik. Zeits.*, **31**, 772 (1930).

[2] Rupp, *Ergeb. Exakt. Naturwiss.*, **9**, 79 (1930).

[3] Lebedeff, *Nature*, **128**, 491 (1931).

[4] Phillips, *Physics*, **2**, 48 (1932).

been used successfully by the authors to obtain diffraction effects from various thin crystalline films is described below.

Figure 5-11 represents a longitudinal section of the apparatus. The central portion is a piece of brass tubing, 2 in. in external diameter with $\frac{1}{8}$-in. walls, and about 15 in. long. Two pumping exits of $\frac{1}{2}$-in. brass pipe are provided, one leading from the region of the cathode and the other from the far side of the collimating diaphragms H_1 and H_2. When a hot filament is used as a cathode, a rapid pump is attached to these exits in order to keep as good a vacuum as possible. As the tube cannot be baked out, gas is evolved during operation which, if it is not removed, will cause a disruptive discharge. It is convenient to have a large stopcock in the vacuum line between the tube and the liquid air trap and pump, for operation with a cold cathode.

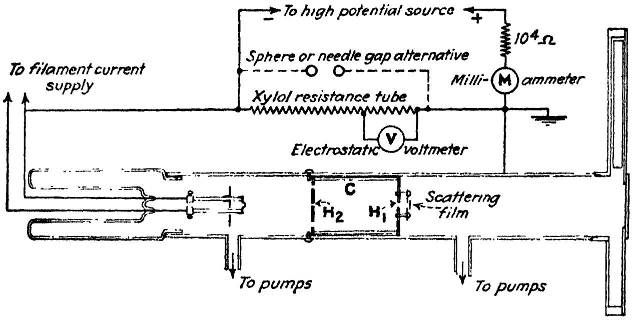

FIG. 5-11.—An electron diffraction apparatus.

The cathode itself may be either a filament as shown in Fig. 5-11, or simply a nickel plate spot-welded to a tungsten rod passing through the glass, to act as a cold cathode in a gas discharge. The filament has the advantage that both the current through the tube and the potential across it may be controlled separately, leading to more stable operation and more uniform velocities of the electrons. It has the disadvantage that a circuit for heating it must be provided, which may have to be operated at a high potential above ground. This can be done with a transformer whose secondary is well insulated, such as an X-ray tube filament transformer, or with isolated storage batteries. A coated filament has been found more satisfactory than a tungsten helix, since it dissipates less heat. Such a filament can be made by spot-welding a thin platinum strip, notched at the center, on to nickel rods which in turn are fastened with set screws or welded to tungsten leads passing through the glass press. If this strip is coated heavily with varnish containing barium and strontium oxides, it will emit electrons copiously at low temperatures and operate many hours. A disk-shaped guard of nickel behind the filament is an advantage; it increases the forward emission and tends to reduce the damage to the filament in case an arc is struck. The disk is welded to one limb of the filament support and contains a hole for the passage of the other. The press containing the cathode is sealed to a glass tube slightly over 2 in. in diameter, the open end of which is made a bit smaller so that it may be sealed with vacuum wax into the brass tube. As this joint becomes warm during operation with either a filament or cold cathode, some provision for cooling it should be made; a water jacket, or a helical coil of lead tubing through which water flows, or a wet cloth cooled by several jets of compressed air may be used. As the brass body of the apparatus is grounded for safety, these arrangements can be made without difficulty.

The diaphragms H_1 and H_2 are 0.35-mm. holes (No. 80 drill) bored in brass sheets carried on the ends of a thick-walled iron cylinder C, which fits closely inside the main tube. The iron affords magnetic shielding for the region between the collimating holes. The distance that this cylinder can be pushed in from the camera end is limited by three screws in the main tube, the screw heads being waxed or soldered to make the joints vacuum tight. The end of the cylinder nearest the filament is pierced by several $\frac{1}{4}$-in. holes near its circumference so that the region between the diaphragms may be rapidly exhausted. The other end supports a thin brass disk pierced by a hole $\frac{1}{16}$ in. in diameter; this disk is held about $\frac{1}{4}$ in. from the diaphragm H_1 by three small brass bolts and acts as a support for the scattering films themselves or for the wire gauze on which the films are placed. As the cylinder is 3 in. long, the maximum divergence of the main electron beam is less than 30 min. of arc. For the purpose of placing the films in position, the cylinder can be removed by means of a rod with a hook on the end which engages one of the bolts holding the film support.

The camera is sealed to the end of the tube with wax. In the simplest form the camera may be a metal cap containing a circular piece of photographic film held in place by clips, but this arrangement has the disadvantage that preliminary visual adjustments cannot be made nor can more than one picture be taken without letting air into the apparatus. A much more convenient arrangement is shown in Fig. 5-11. A metal container holds a shallow film holder which slides vertically in front of the diffraction chamber; when in the extreme upper position, visual observation may be made with the fluorescent glass screen at the back of the camera, while three photographic exposures can be made by allowing the film holder to fall under gravity, by means of a magnetic release. When all the pictures are taken, air is admitted to the apparatus, the wax joint softened, and the camera rotated about the tube axis, thus permitting the film holder to fall back into its original position, in which the camera may be removed and taken to the dark room without endangering the film. As the film holder is $4\frac{1}{4}$ in. long, $3\frac{1}{4}$ by $4\frac{1}{4}$-in. X-ray film may be used conveniently; a strip $1\frac{1}{2}$ in. wide is cut and fed into the holder through the short brass collar and the holder is snapped into the upper position. The camera may then be taken from the dark room and sealed on to the tube.

A section through the camera normal to the tube axis is shown in Fig. 5-12. The plate forming the face of the camera toward the filament is a rolled-brass block 10 by $2\frac{3}{4}$ by $\frac{3}{8}$ in. This is milled out to a depth of $\frac{13}{64}$ in. to within $\frac{1}{4}$ in. of three of the sides and within $\frac{3}{4}$ in. of the side which contains the release mechanism. A small section of this side is also milled out as indicated in the diagram, in order to contain the steel escape catch. This is free to rotate about the pin through its center which holds it in place, and a piece of steel spring presses its upper end toward the middle of the tube in order to engage the notches on the side of the film holder. When a small electromagnet is brought up as indicated, the upper edge of the catch is pulled away so that the film holder drops until the bottom is caught by the lower end of the catch. When the magnet is removed, the catch snaps back and the holder falls farther until the first notch comes up against the upper arm of the catch; the first picture may then be taken. The film holder is a shallow brass tray, the bottom being $4\frac{1}{2}$ by $1\frac{1}{16}$ in. and $\frac{1}{16}$ in. thick; the edges are made of brass rod of square cross section, $\frac{1}{8}$ in. on a side, soldered into place. If the ends of the tray are slightly beveled on the inner side, the film will be more securely held in position. The first point of contact of the holder with the catch should be an extension of the tray, so that the film may be well within the body of the camera when in the position for transport. The brass block forming the main body of the camera is soldered to a short piece of tubing, so that the junction with the diffraction chamber may be made conveniently; the length of this section should not be more than about $\frac{1}{2}$ in., as otherwise the insertion and removal of the photographic film become difficult. The back of the camera is a piece of brass sheeting $\frac{1}{8}$ in. thick. This contains a circular opening $1\frac{1}{2}$ in. in diameter, opposite the main tube, covered with a glass window waxed in place; the inside of the window is painted with fluorescent material in the same manner as has been described in connection with the velocity filter method of determining the ratio e/m in Chap. IV. This screen is very convenient for preliminary adjustment and for visual work at high current densities. The back of the camera is screwed to the edges of the main block, as indicated; a coating of glyptal lacquer or wax renders the joint vacuum tight.

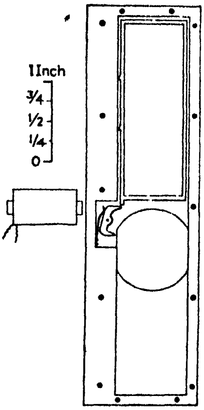

FIG. 5-12.—Details of the camera, with the back plate removed.

In assembling the apparatus, the cylinder C is inserted into the main tube, with no scattering film in place. The glass cathode end is waxed into position. While the wax is still warm the filament should be heated to a dull red and the cathode assembly twisted about until the notch in the filament is in line with the two holes in the collimating cylinder. If a cold cathode is used, a similar adjustment is unnecessary. The distance from the scattering film holder to the end of the main tube is measured with a meter stick; when this is added to the distance from the photographic film to the bevel in the collar of the camera, the length S is obtained.

The cylinder is then removed, a scattering film put in place, and the cylinder returned to position; the camera is sealed on and the system evacuated. When a filament is used, a pressure of less than 10^{-5} mm. Hg should be maintained. It takes several hours, when the tube is first used, to obtain this pressure when the filament is lit, but after continued operation a satisfactory vacuum may be reached in a few minutes after putting on the camera. If a gas discharge is used, with a cold cathode, a pressure of 10^{-5} to 10^{-3} mm. Hg of the residual gas is necessary. As gas continues to be evolved during an exposure with either type of electron source, the tube must remain connected to the pumps; with a cold cathode, the rate of pumping is adjusted to be equal to the rate of gas evolution by means of a stopcock. A constant gas pressure, and hence a constant potential, is most conveniently maintained by observing the voltmeter across the tube and by keeping this reading constant by adjustment of the stopcock; opening it increases the potential drop, while closing it reduces the voltage. Constancy of potential to within 1 or 2 per cent may be maintained by this method.

To observe the diffraction patterns on the fluorescent screen, fairly high currents must be used; a total of several milliamperes from the filament generally suffices. This is measured by a milliammeter, one side of which is connected to the main body of the tube, the other terminal leading through a protective resistance of several thousand ohms to the high-potential source and thence to the cathode. It is not easy, however, to obtain a fairly constant direct current of this amount at high voltages with simple apparatus, so that it is more satisfactory to use smaller currents and to photograph the patterns. With 10,000 to 30,000 volts, satisfactory exposure times with thin scattering films are of the order of a few hundred microampere-minutes. If the film holder is in position for an exposure and an adjustment of the current or potential is desired, a small horseshoe magnet may be clamped near the tube between the filament and the first diaphragm; this prevents electrons from passing through and affecting the plate. To demonstrate that the diffraction patterns are really due to electrons, the magnet may be placed around the tube between the scattering film and the camera; the rings will then be found to be deflected as a whole with comparatively little distortion. If Helmholtz coils are put on either side of the tube over this region, the pattern may be deflected without distortion, and, from a knowledge of the magnetic field strength and the displacement of the pattern, the velocity of the electrons can be readily calculated [by means of Eq. (4-10)] as a check on the velocity determined from the voltmeter.

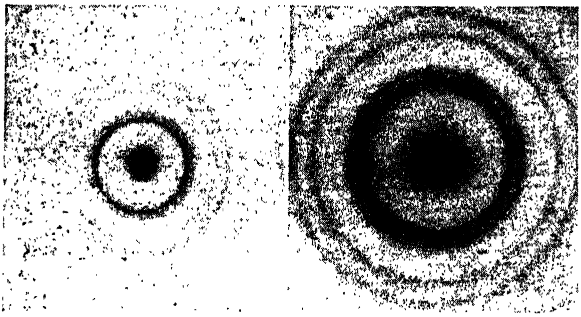

FIG. 5-13.—Electron diffraction patterns through gold films. The larger pattern was formed with 13,500-volt electrons, and the smaller with 36,500-volt electrons.

ANALYSIS OF ELECTRON DIFFRACTION RINGS FROM GOLD
Crystal spacing a (gold) = 4.06×10^{-8} cm. $S = 15.8$ cm.

H	K	L	$\sqrt{H^2+K^2+L^2}$	Weighted mean	Radius, r	$\lambda = \dfrac{ar}{S\sqrt{H^2+K^2+L^2}}$
1	1	1	$\sqrt{3}$	$\sqrt{3}$	0.431 cm.	6.39×10^{-10} cm.
0	0	2	2	2	0.495	6.36
0	2	2	$\sqrt{8}$	$\sqrt{8}$	0.701	6.38
1	1	3	$\sqrt{11}$	$\sqrt{11.25}$	0.827	6.34
2	2	2	$\sqrt{12}$			
0	0	4	4	4	Missing	
1	3	3	$\sqrt{19}$	$\sqrt{19.5}$	1.095	6.37
0	2	4	$\sqrt{20}$			
2	2	4	$\sqrt{24}$	$\sqrt{24}$	1.206	6.32
1	1	5	$\sqrt{27}$	$\sqrt{27}$	1.295	6.40
3	3	3	$\sqrt{27}$			
1	3	5	$\sqrt{35}$	$\sqrt{35.4}$	1.490	6.42
0	0	6	$\sqrt{36}$			
2	4	4	$\sqrt{36}$			

Measured average $\lambda = 6.37 \times 10^{-10}$ cm.

$$\text{Computed } \lambda = \sqrt{\frac{150}{36{,}500}} \times 10^{-8} = 6.41 \times 10^{-10} \text{ cm.}$$

Thin films of mica may be used, yielding patterns of spots similar to those indicated in Fig. 5-6. With sputtered films of molybdenum or gold, circular diffraction images are formed; for the former, the intensity is not uniform around the circumference because of lack of complete randomness of position of the crystal blocks. Rings obtained with gold are shown in the photographic reproduction of Fig. 5-13. The larger pattern was obtained with 13,500-volt electrons and the smaller with 36,500 volts. In the original photograph of the latter, 8 rings are clearly visible, corresponding to 13 different types of crystal planes. The data for the 36,500-volt patterns are shown in the table on page 183, as an example. The agreement shown in this table is well within the accuracy with which the measurements can be made, which is of the order of 1 per cent.

5-10. Potential Sources.—It is difficult to obtain diffraction patterns of this sort with electrons having less than several thousand volts energy, due to the inability of slow electrons to penetrate the film. The most convenient range to use is from 10,000 to 50,000 volts; in this region there are practically no disturbing effects from stray magnetic fields and no difficulty in obtaining sharp rings in a reasonable exposure time from scattering films which can be made readily. At higher potentials the equipment becomes more expensive, and insulation difficulties and the chance of arcing within the tube become more pronounced.

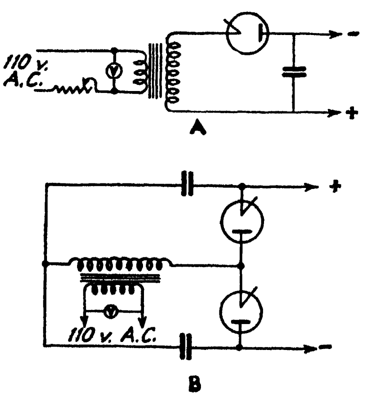

Fig. 5-14.—High-potential circuits with kenotron rectifiers.

The currents necessary are not large, if long exposures are possible. A static machine capable of supplying a microampere can be used, but the exposure time may run into several hours. A circuit with an induction coil and Leyden jars is satisfactory, but as it is essentially the same as a transformer circuit, it will not be described in detail. Possibly the most convenient potential source, if it is available, is an X-ray generator, for the connections to the diffraction tube are identical with those for an X-ray tube. In particular, an X-ray filament transformer is the most convenient source of current for the filament, if a hot cathode is used.

Small 10,000- or 25,000-volt transformers may be employed satisfactorily. Figure 5-14 shows two circuits, half-wave and full-wave rectified, employing kenotron tubes, which are available commercially. As their construction is quite simple, the elements consisting of a nickel plate and a 5- or 10-mil tungsten filament, satisfactory rectifying tubes can be made in the laboratory. For use with high potentials the elements should be sealed into arms at opposite ends of the bulb. The tubes and metal parts should be well baked out and operated for some time on the pumps before sealing off, to insure good vacuum conditions.

The capacities may be Leyden jars or mica condensers capable of withstanding the applied potentials. Satisfactory condensers may be made with tin foil or thin copper sheeting, separated by micanite or micarta about 1 mm. thick. The dielectric plates should extend several inches beyond the metal sheets, and corona loss can be decreased by coating them with shellac or immersing them in a tank of transformer oil. The necessary capacity depends on the frequency of the potential source, the voltage and current to be used, and the percentage fluctuation to be permitted in the potential across the diffraction tube. Thus in the half-wave circuit of Fig. 5-14*A*, let us assume that the mean current flowing from the condenser through the diffraction apparatus is given by I. If Δt is the time of one cycle of the alternating current, the total charge leaving the condenser per cycle is $I\Delta t$, and this must equal $C\Delta V$, where C is the capacity and ΔV the change or fluctuation in the potential across the apparatus during this time. Therefore

$$\frac{\Delta V}{V} = \frac{I\Delta t}{VC} \tag{5-43}$$

If a current of 50 microamp. at 20,000 volts is drawn, and if 60-cycle alternating-current supply is used, a capacity of 0.0042 μf. will prevent the potential from fluctuating by more than 1 per cent. The full-wave rectifier of Fig. 5-14*B* produces double the transformer voltage across the diffraction tube, and if each of the condensers has the above capacity, 50 microamp. may be drawn at 40,000 volts with a 1 per cent fluctuation.

The voltage adjustment is made by means of a rheostat in the primary circuit of the transformer. From the readings of a voltmeter across the primary, and a knowledge of the turn ratio in primary and secondary windings, a rough estimate of the potential across the diffraction tube can be made. This is subject to a large error, so there should be a potential-measuring device across the tube itself. An ordinary voltmeter is out of the question, as even one with a 5,000,000-ohm resistance would draw several milliamperes. The simplest, though not very accurate, method of determining the potential is to use a needle point or sphere gap across the tube terminals, as shown in Fig. 5-11. The sparking potential for needle gaps depends considerably on the individual points and on atmospheric conditions; spheres are almost independent of the weather. A disadvantage of this method is that the voltage is known only when a reading is taken; fluctuations are not recorded. Tables of sparking potentials, taken from Peek,[1] are given on page 186.

An electrostatic voltmeter is quite satisfactory, as it draws no current. These meters may be purchased already calibrated or they may be constructed quite simply[1] and calibrated over the desired range with a galvanometer and a set of accurate high resistances of the wire-wound type. A very simple expedient which has given satisfactory results is the use of a low-range electrostatic voltmeter (which can be calibrated accurately against an ordinary laboratory voltmeter up to, say, 2,000 volts) to measure a known fraction of the potential drop across a tube containing a high-resistance liquid such as xylol. This glass tube,

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[1] PEEK, "Dielectric Phenomena in High Voltage Engineering," pp. 116ff., McGraw-Hill (1929).

SPARKING POTENTIALS IN KILOVOLTS (EFFECTIVE)*

Gap, centimeters	No. 00 needles 25°C. 760 mm. average humidity	Diameter of spheres (one grounded)		
		2.0 cm.	6.25 cm.	12.5 cm.
0.2	....	5.6	....	5.5
0.3	....	8.0	....	8.0
0.4	....	10.3	10.0	10.0
0.5	....	12.5	12.0	12.0
0.6	....	14.6		
0.7	....	16.7		
0.8	....	18.6		
0.9	....	20.2		
1.0	8.0	21.7	22.5	22.0
1.2	10.0	24.4		
1.4	11.5	26.4	30.0	30.0
1.6	13.0	28.2		
1.8	14.5	30.0		
2.0	16.0	....	41.0	41.0
3.0	23.0	....	56.0	59.0
4.0	29.0	....	66.0	75.0
5.0	34.5	....	73.0	89.0
6.0	39.3	....	79.0	102.0
7.0	43.0	....	83.0	112.0
8.0	47.0	....	88.0	120.0
9.0	50.0	....	90.5	128.0
10.0	53.5	....	93.0	135.0
12.0	60.3	....	....	147.0
15.0	70.3	....	....	160.0
17.5	78.2	....	....	168.0
20.0	....	....	....	174.0

* Effective or root mean square sparking potentials depend to a certain extent on the frequency; high-frequency sparking potentials are about 83 per cent of the above values.

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[1] TERRILL and ULREY, "X-Ray Technology," pp. 117 ff., Van Nostrand (1930).

which should be of uniform bore about 1 cm. in diameter, has three small tungsten electrodes sealed into it, the spacing between them being 3 and 57 cm. It is clamped in a horizontal position, one end electrode being connected to the filament, the other to the brass case of the diffraction tube; the electrostatic voltmeter is shunted across the latter electrode and the one 3 cm. away. The true potential is thus given by the voltmeter reading multiplied by 20.

5-11. Preparation of Scattering Films.—The technique of preparing sufficiently thin films to obtain clear and sharp diffraction patterns warrants a brief discussion. In order that the background shall not be darkened by multiple scattering, it has been shown by Schöbitz[1] that the films should be between 10^{-5} and 10^{-6} cm. thick. It is not only difficult to prepare films thinner than 10^{-6} cm., but the diffraction patterns become fainter. Various techniques may be employed for preparing these films, excellent accounts of which have been given by Thomson[2] and by Ponte.[3] The method of reducing commercial films to the desired thickness by various reagents has been found very difficult and much less satisfactory than the formation of the films by evaporation or by cathodic sputtering on glass, as described in Appendix B. The colors of these films as seen by transmitted light are characteristic of the metals—gold appears a very pale green. When the glass has been removed from the sputtering chamber, it is given a thin coat of Duco lacquer; when this is dry but before it becomes brittle, it is stripped from the glass, carrying the metal film with it. This composite film may then be stored and portions of it used as required.

A very convenient support for the film has been found to be a circular piece of platinum gauze 1 cm. in diameter and of about 0.5-mm. mesh. A heavy platinum wire may be welded around the circumference by tapping with a hammer in a blow-torch flame. Such a framework can be readily cleaned and used for any type of film. A piece of the composite film about the size of the gauze is cut and laid on the frame in a watch glass. Ethyl or amyl acetate is then slowly allowed to flow from a dropper or pipette into the watch glass until it is full. Gradually the Duco lacquer is dissolved away, and, if care is used, the metal film remains over the platinum frame and adheres to it slightly. After several washings in the solvent, the framework can be withdrawn by grasping it with tweezers and sliding it along the bottom of the watch glass to one edge. Breakage of the film over one or more of the meshes may occur during this process or when the film dries, but as any of the meshes may be adjusted over the hole in the disk in front of the second collimating diaphragm, a good portion is almost certain to be obtained. The platinum gauze may be held in place in the scattering chamber by metal clips or by one or two drops of wax applied with a small soldering iron.

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[1] Schöbitz, *Physik. Zeits.*, **32**, 37 (1931).

[2] Thomson, G. P., "The Wave Mechanics of Free Electrons," pp. 74*ff.*, McGraw-Hill (1930).

[3] Ponte, *Ann. Physique*. **13**, 395 (1930).

The platinum-mesh support may also be found convenient if substances other than metal films are to be investigated. A small piece of magnesium, zinc, or cadmium introduced into an oxygen flame will burn brilliantly emitting clouds of white oxide. If the platinum frame is held over this flame the wires become coated with the oxide, and when one of the wires is then mounted in line with the collimating diaphragms, diffraction patterns due to these oxides may be obtained. This arrangement requires longer exposure times, as not all of the electrons are effective in producing the diffraction pattern.

The mesh support may be used with thin mica films, or these may be mounted directly on the brass disk with a bit of wax. They must be very thin; otherwise a pattern of lines will be obtained instead of a simple two-dimensional grating pattern. These line pictures are described by Kikuchi[1] and by Thomson;[2] they will not be obtained if the mica films are less than one or two times 10^{-5} cm. thick. To produce such films, mica sheet is split by the insertion of a needle along the edge. As thinner and thinner films are obtained they may be tested by inserting them in one arm of an interferometer adjusted for white light fringes. It is difficult to obtain mica sheets several millimeters square thin enough so that the shift of the black fringe is less than 8 or 10 yellow fringes, and these are too thick to give two-dimensional lattice patterns. However, portions of these films will be sufficiently thin to cause a displacement of less than one yellow fringe, and these parts may be used satisfactorily.

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[1] KIKUCHI, *Physik. Zeits.*, **31,** 777 (1930).

[2] THOMSON, G. P., "The Wave Mechanics of Free Electrons," McGraw-Hill (1930).

CHAPTER VI

THERMIONIC AND PHOTOELECTRIC EFFECTS

6-1. Introduction.—In the course of the previous chapters various experimental arrangements have been described for the production of electrons and ions. The processes by which these electrified particles are produced are of fundamental importance for the understanding of the interactions between photons, electrons, and atomic systems. For purposes of discussion these ionizing mechanisms may roughly be divided into four classes: (*a*) thermal ionization; (*b*) ionization by collision with a charged particle; (*c*) ionization at collision with an atom which is possessed of a certain amount of disposable energy, *i.e.*, a so-called excited atom; (*d*) ionization by radiation. Ions are generated by these processes both in the body of a gas and also on exposed surfaces. While these four mechanisms may be considered as fundamentally the same, the exact process and its relative importance depend very greatly on whether it is taking place in the body of a gas in a discharge tube or on the surfaces of the electrodes. As the phenomena in the former case are in general rather less complex, their interpretation is simpler, and these elementary processes of excitation and ionization of a gas or vapor will be taken up in a later chapter. Here we shall confine ourselves to the first and fourth of the above processes when occurring at metallic surfaces, namely the emission of electrons under the influence of heat and radiation. The other two processes which involve the liberation of electrons or ions from surfaces bombarded with material particles also play very important rôles in connection with gas discharges, but these phenomena are still very incompletely understood. An attempt to consider the subject of gas discharges would lead us far beyond the scope of this book. A detailed application of the ionizing mechanisms outlined above to the problems of the conduction of electricity in gases is to be found in the treatises by Seeliger,[1] Compton and Langmuir,[2] Thomson[3] and Darrow.[4]

6-2. Electron Theory of Metallic Crystals.—From various lines of evidence such as crystallography, the diffraction of X-rays and of electrons, the phenomena of electrical and thermal conduction, and thermionic and photoelectric emission, we are able to build up a physical concept of a crystal. A small element of a crystal is apparently a regular arrangement of atoms composing a so-called space lattice, of which various types are possible. An ordinary crystalline sample is generally not a perfect lattice structure but is composed of a great number of small crystal blocks oriented more or less at random with respect to one another. Even the specially prepared samples known as single crystals, in which the regularity is apparently as homogeneous and perfect as possible, may not in fact be considered a truly perfect lattice, for all the distances between adjacent atoms along one axis are not exactly equal. Thermal motion of the atoms alters to some extent the regularity, and furthermore it has been shown that a completely regular arrangement does not represent a true minimum of potential energy. Such a minimum does exist if there are approximately equally spaced planes, a few thousand atoms apart, of greater density than the average, distributed through the crystal.[1] These theoretical predictions have received experimental confirmation,[2] and hence our conception of a single crystal is that of a coarse-grained lattice formed by these planes of greater density superposed on the fine-grained atomic or ionic lattice.

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[1] SEELIGER, "Physik der Gasentladung," Barth (1927).

[2] COMPTON and LANGMUIR, *Rev. Mod. Phys.*, **2**, 123 (1930); **3**, 191 (1931).

[3] THOMSON, J. J. and G. P., "Conduction of Electricity through Gases," 3d. ed., Cambridge University Press (1928).

[4] DARROW, "Electrical Phenomena in Gases," Williams & Wilkins (1932).

The distance between atomic centers is of the order of magnitude of 10^{-8} cm. This is the same general size as the effective diameter of an atom as a whole. Atoms themselves are of a very open nature, the central nucleus having an effective radius of the order of 10^{-13} cm., only 1/100,000 of the dimensions of the entire atom. Therefore the distances between the positively charged nuclei in a crystal are very much greater than the size of the nucleus itself. The electrons of the atomic systems occupy the region between the regularly spaced nuclei and remain under the influence of their fields of force. It is difficult to specify accurately the strength of this binding, but the existence of X-ray line spectra indicates that the greater number of electrons are bound quite tightly to the individual atomic centers. A few electrons, however, probably one or two per atom, appear not to be definitely associated with any particular nucleus when in a metallic crystal (as opposed to the state of affairs in a gas, where each atom has a particular company of electrons all its own). These orphan electrons are presumably those which are responsible for the electrical and thermal conductivity of metals.

Arguments can be advanced to show that the influence of the nuclei on these semifree electrons can be neither extremely large nor completely negligible. If there were no interaction at all, the laws of the conservation of energy and momentum would be violated when an electron absorbs a photon, as in the photoelectric effect. If a photon of energy $h\nu$ and momentum $h\nu/c$ were completely absorbed by an entirely free electron, initially at rest, the conservation of energy would require

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[1] Zwicky, *Proc. Nat. Acad. Sci.*, **15**, 253, 816 (1929); **16**, 211 (1930).

[2] Goetz, *Proc. Nat. Acad. Sci.*, **16**, 99 (1930).

$$h\nu = mc^2 - m_0c^2$$

where mc^2 is the relativistic expression for the subsequent energy of the electron by Eq. (1-31). Conservation of momentum would necessitate

$$\frac{h\nu}{c} = mv$$

from which we discover that the resultant velocity of the electron would be $v = c$, an impossible result. If, however, we assume that the electron is connected in some way to the nucleus, which participates in the collision and which thus acquires a kinetic energy E and a momentum p, the two equations become

$$h\nu = mc^2 - m_0c^2 + E$$

and

$$\frac{h\nu}{c} = mv + p$$

whence we find to terms in E/mc^2 and u^2/m^2c^2

$$v \cong -\frac{p}{m_0} + \left(\frac{E}{m_0c^2} - \frac{p^2}{m_0{}^2c^2}\right)c$$

which is entirely reasonable. On the other hand, it cannot be that the forces between nuclei and electrons are extremely large, for then the phenomena of metallic conduction could not be as observed. The experiments of Tolman and others[1] have definitely shown that the conduction current in a metal is carried by electrons; if they were strongly bound to the nuclei, there would probably be some minimum field which would have to be applied to a metal before any current would flow at all, *i.e.*, Ohm's law would not be true for small currents. However, this law does hold even for extremely minute currents, and consequently the interaction between the electrons and the crystal lattice must be very weak.

We may therefore consider these so-called free electrons as moving through the lattice structure in a comparatively unhindered way. If we were endeavoring to develop a rigorous theory of metal crystals we should have to consider the wave nature of the electrons, their interaction with the lattice centers, the thermal motion and irregularities of these centers, and many other points which would be far beyond the scope of this presentation. Attempts to develop a theory along these lines have been made by Bloch.[2] An exposition of the general experimental and theoretical status of our knowledge of the structure of metals may be found in the work of Hume-Rothery.[1] We shall adopt a simpler point of view, but one which will yield us results of sufficient accuracy for our purpose. We shall consider that the free electrons constitute what amounts to an "electron gas" permeating the crystal lattice; under the influence of an applied electric field this gas drifts through the crystal, giving rise to the observed conduction current. The motion is not entirely free, for it is retarded by the lattice centers, this interference constituting the ohmic resistance. The average distance traversed by an electron between collisions appears to be quite large—of the order of 600 times the distance between neighboring nuclei—so we may expect this simple picture to give quite satisfactory results.

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[1] TOLMAN and STEWART, *Phys. Rev.*, **8**, 97 (1916); **9**, 164 (1917); TOLMAN, KARRER, and GUERNSEY, *Phys. Rev.*, **21**, 525 (1923).

[2] BLOCH, *Zeits. Physik*, **52**, 555 (1928); **59**, 208 (1929).

The energies of the individual electrons which make up this ensemble within the crystal lattice are not all the same. In accordance with the classical statistical theory of an ordinary atomic gas the number of atoms per unit volume having momentum components between p_x and $p_x + dp_x$, p_y and $p_y + dp_y$, and p_z and $p_z + dp_z$ is given by

$$N_p dp = Ae^{-\frac{\epsilon}{kT}} dp_x \, dp_y \, dp_z$$

where A is a constant, T is the absolute temperature, k is Boltzmann's constant, and ϵ is the energy corresponding to the momentum components p_x, p_y, and p_z; *i.e.*, $\epsilon = (p_x^2 + p_y^2 + p_z^2)/2m$. It was suggested by Sommerfeld[2] from theoretical considerations that this expression is not applicable to an assembly of electrons but that the distribution function is rather of the form

$$N_p dp = \frac{2}{h^3} \frac{1}{e^{-\frac{(W-\epsilon)}{kT}} + 1} dp_x dp_y dp_z \tag{6-1}$$

which is known as the Fermi-Dirac distribution. W is a constant which depends primarily on the number of electrons per unit volume and certain of the fundamental physical constants. This expression yields much more satisfactory agreement with the observed physical phenomena, such as the specific heats of metals, electrical conduction, thermal conduction, etc., than the classical form, and we shall adopt it as a starting point.

The forces which retain the electrons within the metal may be represented by a "potential wall" at the crystal boundary. This is sufficiently high so that at ordinary temperatures practically none of the electrons have sufficient energy to surmount it. If the temperature is raised, however, some of the thermal energy is imparted to the electrons and certain of them gain sufficient energy to escape from the crystal. This constitutes thermionic emission. If light is incident on the surface of the metal, the energy carried by a photon may be absorbed by an electron which is thus enabled to surmount the potential barrier and escape. This is the mechanism of photoelectric emission.

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[1] HUME-ROTHERY, "The Metallic State," Oxford University Press (1931).

[2] SOMMERFELD, *Zeits. Physik*, **47**, 1 (1928).

The value of the constant W appropriate for small masses, low temperatures, and large densities is given to a first approximation by

$$W = \frac{h^2}{2m}\left(\frac{3N}{8\pi}\right)^{\frac{2}{3}} \tag{6-2}$$

where N is the number of particles per cubic centimeter. If we consider, for example, the case of tungsten and assume one free electron per atom, we have $N = 6.1 \times 10^{22}$. Writing the mass of an electron as $m = 9 \times 10^{-28}$, Boltzmann's constant as $k = 1.37 \times 10^{-16}$, the Planck constant as $h = 6.55 \times 10^{-27}$, and taking $T = 300°$ Abs. we find:

$$\frac{W}{kT} = \frac{8.91 \times 10^{-12}}{1.37 \times 10^{-16} \times 300} = 216$$

Even for temperatures as high as 3000° Abs., W/kT is large and $e^{-\frac{W}{kT}}$ consequently very small, so that the effect of the temperature on the density distribution function is not very pronounced. If we plot N_p, given by Eq. (6-1) as a function of the energy for the three temperatures 0°, 300°, and 3000° Abs. we obtain the curves shown in Fig. 6-1. It is observed that for $T = 0°$ we have the same number of electrons in each momentum region, dp, from $\epsilon = 0$ to $\epsilon = W = 8.91 \times 10^{-12}$ erg. A sharp discontinuity then occurs. There are no electrons with greater energies than W, for when the critical value $\epsilon = W$ is reached the term $e^{-\frac{W-\epsilon}{k \cdot 0}}$ changes from zero to infinity. This means that at absolute zero the electrons have settled down and filled all the momentum regions corresponding to the smallest energies. At higher temperatures the situation is not greatly altered; most of the electrons retain the same energy

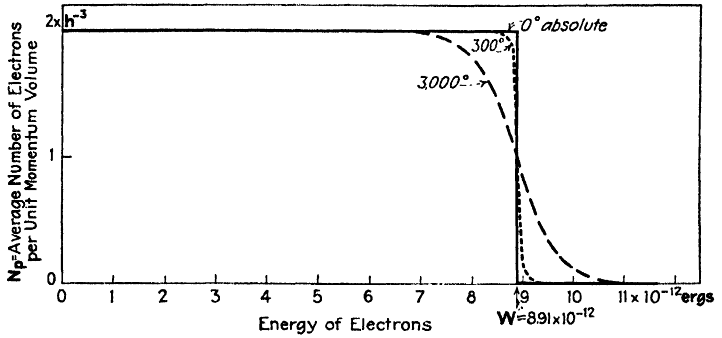

Fig. 6-1.—Diagram showing the density of free electrons in momentum coordinates, according to the Fermi-Dirac statistics. The numerical values are given for tungsten, assuming one free electron per atom, but the general shape of the curve is the same for all elements.

as at zero, but a few of them have moved out to regions corresponding to a higher energy content. Thus a higher temperature has little influence on the majority of the electrons, but those few having the greatest kinetic energies undergo an increase in energy. We shall see that this small effect is responsible for thermionic emission and the other changes in the properties of a metal which depend on the electron-gas energy.

If we wish to consider N_ϵ (the density in an energy range) rather than N_p (the density in a momentum region), we must calculate the number of differential elements of volume $dp_x\,dp_y\,dp_z$ which lie in the energy range $d\epsilon$. Since $2m\epsilon = p_x^2 + p_y^2 + p_z^2$, the range $d\epsilon$ contains the number of elements $dp_x\,dp_y\,dp_z$ included in a spherical shell of radius $(2m\epsilon)^{\frac{1}{2}}$ and thickness $d(2m\epsilon)^{\frac{1}{2}}$, *i.e.*

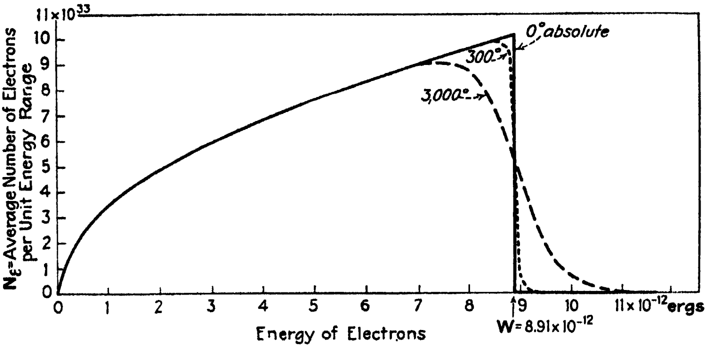

FIG. 6-2.—A diagram showing the average number of free electrons per unit energy range for tungsten, on the Fermi-Dirac statistics.

$$\frac{2\pi(2m)^{\frac{3}{2}}\epsilon^{\frac{1}{2}}\,d\epsilon}{dp_x\,dp_y\,dp_z}$$

Hence

$$N_\epsilon\,d\epsilon = N_pC\epsilon^{\frac{1}{2}}\,d\epsilon \tag{6-3}$$

where $C = 2\pi(2m)^{\frac{3}{2}}$. Since N_p is constant except in the neighborhood of W, we see that N_ϵ increases parabolically with ϵ. This shows how the number of electrons having a certain energy varies with the magnitude of that energy. Figure 6-2 is a graph of N_ϵ against ϵ; it is observed that the temperature has but a small effect on the distribution.

Even at 0° Abs., there are many electrons with energies between 8 and 8.9×10^{-12} erg. When an electron falls through a potential difference of 1 volt, it acquires an energy of $4.77 \times 10^{-10}/300 = 1.59 \times 10^{-12}$ erg, so that the electrons in the above range have energies corresponding to 5 and 5.6 volts. If these electrons remain in the metal at low temperatures, it must mean that the retaining potential wall of the crystal structure is greater than this amount. Such a potential barrier is higher than we would have had to assume if we had calculated the energy distribution of the electrons on the basis of the classical statistics. If a larger number of free electrons per atom were assumed, we should have to assume a still higher potential wall. On the basis of the experiments of Davisson and Germer mentioned in the preceding chapter, it appears that the potential barrier, for nickel, may be as high as 18 or 20 volts, which would retain 2 or 3 free electrons per atom.

Since the distribution in energy content of the electrons changes so little with the temperature, as Fig. 6-2 indicates, we see that the electrons can contribute only very slightly to the specific heat of the metal. It is thus apparent that the Fermi-Dirac statistics applied to electrons leads to a very different result than if the classical statistics had been used. In the latter case we would be led to the *principle of the equipartition of energy*, by which every particle of a system shares equally in thermal energy; this concept was used, in a disguised form, when discussing Brownian motion, and Eq. (3-10) was the result. The values of the specific heats, and the thermal and electrical conductivities calculated on the Fermi-Dirac basis, are in much better accord with experimental values than are the same quantities derived from the classical statistics. This is good evidence that the assumptions that have been made are justified.

6-3. Thermionic Emission.—While it had been known for a great many years that bodies were unable to retain an electric charge if they were raised to a sufficiently high temperature, a thorough investigation of the phenomenon was not undertaken until the end of the last century. The first of this work was performed by Elster and Geitel[1] between 1880 and 1890, who studied the rate at which an electrode in the neighborhood of a heated wire acquired an electric charge. The experiments were performed in the presence of gases at fairly high pressures, and, as a consequence of the large number of variables involved, the results were complicated and difficult to interpret. The existence of many of the fundamental thermionic phenomena was, however, established. The fact that an incandescent body emits electricity, even in the best obtainable vacuum, was observed by Edison and later investigated by Fleming.[2] The main contribution to the subject was made by Richardson[3] in the years immediately following 1900.

It has been shown experimentally that both positive and negative electricity can be emitted by incandescent bodies under the best vacuum conditions. The emission of positive ions from a surface contaminated with almost any salt is found to decrease steadily with time. On the other hand, it is found that though the emission of negative electricity at first varies with the surface conditions, it finally settles down to a constant and reproducible value which is a function of the temperature, the applied electric field, and the nature of the emitting surface. The measurements of the charge and the ratio of the charge to mass of these negative particles, as described previously, indicates definitely that they are electrons, identical in these respects no matter what their source. It is the dependence of the electron emission on the temperature, the applied electric field, and on the conditions of the surface, with which we shall be immediately concerned.

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[1] Elster and Geitel, Series of papers in *Ann. Physik* (1889–1892).

[2] Fleming, *Proc. Roy. Soc.*, **47**, 118 (1890); *Phil. Mag.*, **42**, 52 (1896).

[3] Richardson, "Emission of Electricity from Hot Bodies." Longmans (1916).

Let us now suppose, as a first approximation, that the electrons which escape from the metal are those which reach the surface with a momentum component normal to it sufficient to permit them to surmount the potential barrier. From Eq. (6-1) we see that the number of electrons having momentum components in the region $dp_x\, dp_y\, dp_z$ is given by

$$N_p dp = \frac{2}{h^3} \frac{1}{e^{-\left(\frac{W-\epsilon}{kT}\right)} + 1} dp_x\, dp_y\, dp_z$$

where $\epsilon = (p_x^2 + p_y^2 + p_z^2)/2m$. If the boundary is parallel to the yz plane, and if we neglect electron collisions within the metal, the number of electrons with a momentum p_x reaching the wall per second will be equal to the above expression multiplied by the x-velocity component, $v_x = p_x/m$

$$N_p v_x dp = \frac{2}{mh^3} \frac{p_x}{e^{-\left(\frac{W-\epsilon}{kT}\right)} + 1} dp_x\, dp_y\, dp_z \qquad (6\text{-}4)$$

The current per unit area leaving the surface will be this number multiplied by the charge of the electron and integrated for p_y and p_z from $-\infty$ to $+\infty$, and for p_x from some minimum value, say p_x', to $+\infty$. The presence of the potential barrier requires that p_x' be some positive quantity, of magnitude yet unknown.

$$I = \frac{2e}{mh^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{p_x'}^{\infty} \frac{p_x}{e^{-\left(\frac{W-\epsilon}{kT}\right)} + 1} dp_x\, dp_y\, dp_z \qquad (6\text{-}5)$$

As the electrons that can escape from the retaining potential wall are those whose energies are considerably greater than W; the exponential term is then large compared to unity, which we neglect, and so may write

$$I = \frac{2e}{mh^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{p_x'}^{\infty} p_x e^{\frac{W}{kT}} e^{-\left(\frac{p_x^2 + p_y^2 + p_z^2}{2mkT}\right)} dp_x\, dp_y\, dp_z \qquad (6\text{-}6)$$

This expression may be integrated in three separate steps, one for each variable, and, remembering that

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

we obtain

$$I = 2\left(\frac{2\pi mek^2}{h^3}\right)T^2e^{-\left(\frac{W_a - W}{kT}\right)} \tag{6-7}$$

where W_a is written for $p_x'^2/2m$. The quantity W_a so defined is the height of the potential wall expressed in energy units. The current per unit area in electrostatic units, if the charge e is given in those units, is then

$$I = 2A_0T^2e^{-\frac{e\phi}{kT}} \tag{6-8}$$

where we have written $e\phi = W_a - W$. A_0 is an absolute constant as it depends only on m, e, k, and h; its value is 1.806×10^{11} e.s.u. cm.$^{-2}$ deg.$^{-2}$ sec.$^{-1}$ or 60.2 amp. cm.$^{-2}$ deg.$^{-2}$ The quantity $e\phi$ is the excess over the maximum energy of an electron at 0° Abs. which it is necessary for an electron to possess if it is to surmount the retaining potential wall. This quantity $e\phi$ is known as the *work function* of the surface and is expressed in electron volts; sometimes this name is loosely applied to merely the potential ϕ.

As we shall see, this expression for the dependence of thermionic current upon temperature is in very good agreement with experiment. The exponential form of the equation has been verified over possibly as wide a range of the variables as any physical law. The term T^2 is of much less importance in determining the form of the function; in fact, it has been difficult to show experimentally that the correct expression contains the temperature to the second power rather than to the one-half power, as first suggested by Richardson. The value of the constant factor represented by $2A_0$ still presents some difficulties; while for a few materials the value of this constant as predicted above seems satisfactory, there are several instances, notably in the case of platinum, in which the experimental value differs widely from the theoretical. Several suggestions have been made to account for these discrepancies, but a detailed examination of them would detain us too long. It should, however, be mentioned that on the conception of electrons as waves falling on the potential wall, there is a certain probability of transmission and of reflection. Thus Eq. (6-8) should be multiplied by a mean transmission coefficient which may range from zero to unity. Such a coefficient would account for observed values of the current that are too small, but not for those that are too large. A full account of the present theoretical and experimental status of thermionic emission has been given by Dushman.[1]

6-4. Contact Potential.—If the energy value W and the potential barrier W_a are not the same for all metals, it is readily seen that an effective potential difference will exist between two metal surfaces. Suppose we have two plates of different metals in a vacuum, joined by a wire. If we wish to carry an electron from one plate to the other across the vacuum and back through the wire, we must first do work $(W_a - W)$ to raise the electron from the interior of the first metal, where its energy was W, to the top of the potential barrier, of energy W_a. We recover energy of the amount $(W_a' - W')$ in letting the electron down over the potential wall of the other plate, in the interior of which it has the energy W'. The trip back through the wire to the energy condition W in the first plate requires practically no work, since the Peltier coefficient of the junction of two dissimilar metals is of the order of 0.001 volt. We shall neglect this quantity and the ohmic resistance. If the potential barriers W_a and W_a' are of the same height, no energy is expended in crossing the vacuum from the top of one wall to the top of the other, but if W_a' is greater than W_a, for instance, a quantity of work which we may call eV_c must be expended in crossing the gap, in order to satisfy the conservation of energy. Thus

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[1] Dushman, *Rev. Mod. Phys.*, **2**, 381 (1930).

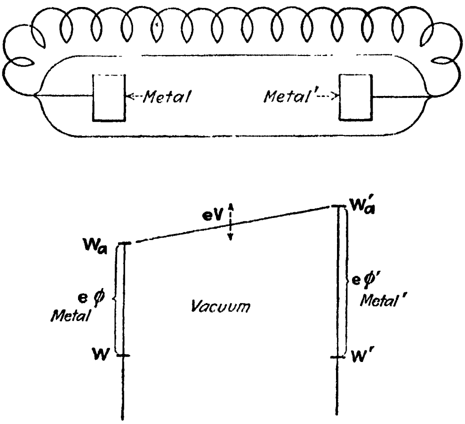

FIG. 6-3.—A diagram indicating the relative energy conditions of two metal electrodes having different work functions. The presence of a contact potential causes a potential difference V to exist between the surfaces, although there is no battery in the circuit.

$$(W_a - W) + eV_c = (W_a' - W')$$

or

$$eV_c = e\phi' - e\phi \tag{6-9}$$

This quantity V_c, which is equal to the difference between the ϕ's for the two metals, is known as the *contact potential difference.* It depends upon the nature of the surfaces as well as upon the type of metal, and hence it is subject to change by any of the numerous factors affecting surface conditions. It is a very inconvenient and disturbing quantity, for all experimentally measured differences in potential between electrodes, such as those made with a voltmeter or potentiometer, merely determine the potential difference, if any, between the interior energy conditions W and W' and tell us nothing of what we really want to know in many cases, namely, the actual potential between the surfaces of the electrodes. This knowledge is particularly necessary in measurements of critical potentials and photoelectric energy distributions, as we shall see later, so that the contact potential must either be avoided or a separate measurement made of it at the time, by methods that will be discussed in due course.

6-5. Space Charge.—In the discussion of thermionic electron currents it was assumed that all the electrons that left the hot metal were recorded by the current measuring device. This is not strictly true, for at small potential differences between the filament and plate (of the order of a few volts), many electrons leaving the filament return to it again and do not reach the collector. These form a negatively charged cloud near the filament and hence produce a large potential mound which other electrons from the filament are unable to surmount. The dependence of the actually measured current upon the applied voltage may be calculated for certain simple arrangements of the emitting and collecting surfaces. The potential distribution throughout any region may be obtained in terms of the charge density, and the current may be expressed in terms of this density and its velocity, the latter being itself a function of the potential. Therefore the current can be calculated in terms of the potentials at the boundaries of the region. It can be shown that a current limited by this so-called space charge of electrons is always proportional to the three-halves power of the potential difference between the emitting and collecting surfaces, but the constant of proportionality depends on the geometrical arrangement of the electrodes.

In the case of an emitter in the form of a fine wire of radius a, surrounded by a concentric collecting cylinder of radius b, we may conveniently use cylindrical coordinates, in which Poisson's equation

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = -4\pi\rho \tag{6-10}$$

becomes

$$\frac{d^2 V}{dr^2} + \frac{1}{r}\frac{dV}{dr} = -4\pi\rho = 4\pi ne \tag{6-11}$$

since the potential V is independent of z and the angle variable; here n is the number of electrons per unit volume at a distance r from the axis. The current per unit length in electrostatic units, or the charge passing per second through unit length of a cylindrical shell of radius r, is

$$I = 2\pi r\rho v = 2\pi rnev \tag{6-12}$$

If the initial velocity of the electrons on leaving the filament may be neglected, we may write

$$eV = \frac{mv^2}{2} \tag{6-13}$$

Eliminating n and v from these equations we obtain

$$\frac{d^2V}{dr^2} + \frac{1}{r}\frac{dV}{dr} = \frac{I}{r}\left(\frac{2m}{e}\right)^{\frac{1}{2}}\frac{1}{V^{\frac{1}{2}}} \tag{6-14}$$

Rather than attempt a general solution of this equation, we may assume a solution in the form $V = Ar^{\alpha}$, where A and α are undetermined constants. Substituting this in Eq. (6-14), we find

$$A^{\frac{3}{2}}\alpha^2 r^{\frac{(3\alpha-2)}{2}} = I\left(\frac{2m}{e}\right)^{\frac{1}{2}} \tag{6-15}$$

Since the current through the cylindrical shell must be the same at all distances from the axis, the right side does not depend on r, and hence the exponent of r on the left side must equal zero. This gives $3\alpha - 2 = 0$ or $\alpha = \frac{2}{3}$ and hence by Eq. (6-15)

$$A^{\frac{3}{2}} = \frac{9I}{4}\left(\frac{2m}{e}\right)^{\frac{1}{2}}$$

and

$$V = \left[\frac{9I}{4}\left(\frac{2m}{e}\right)^{\frac{1}{2}} r\right]^{\frac{2}{3}}$$

This makes V, and hence v, small for small values for r. Although neither of these vanishes for $r = a$, as they should, this is still a satisfactory solution. Solving the last equation for I,

$$I = \frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\frac{V^{\frac{3}{2}}}{b} \tag{6-16}$$

where we have replaced r by b, and hence V is here the potential difference between the surfaces of the electrodes. All quantities are expressed in electrostatic units. This expression may be expected to be valid for small currents, *i.e.*, for I less than Ne, where N is the number of electrons emitted per second per centimeter length of the filament. The maximum value of the current Ne, when the applied potential is so large that the space-charge cloud of electrons is swept away before it becomes formed, is known as the saturation current, and it is this latter whose dependence on temperature we have calculated in obtaining Eq. (6-8). As may be seen from Eq. (6-16) we can calculate e/m from a measurement of the thermionic current when limited by space charge, if we know the radius of the collecting cylinder and the actual potential between the electrodes, *i.e.*, the applied potential corrected for the contact effect. This method of finding e/m, however, is not capable of great accuracy. Putting in the accepted value of e/m, expressing the current in amperes per centimeter length of filament, the potential in volts and the radius of the cylinder in centimeters, we obtain

$$I = 1.46 \times 10^{-5}\frac{V^{\frac{3}{2}}}{b} \tag{6-17}$$

6-6. Velocity Distribution of Thermoelectrons.—It is observed experimentally that electrons are emitted from a hot body with a wide range of initial velocities, for even when the potential between the emitting and collecting electrodes is slightly retarding (when corrected for contact potential) some electrons are nevertheless received. The number of electrons with a particular velocity v may be found from the magnitude of the current for a retarding potential V through the relations $I = Nev$ and $mv^2/2 = eV$. As the retarding potential is reduced, the slower electrons are able to advance against it, until finally when the region between the electrodes is field free all the emitted electrons reach the plate. In practice, however, the presence of space charge upsets these ideal conditions, so that it is generally possible to investigate the velocity distribution only over the range of the fastest electrons and for relatively low temperatures where the currents are so small that space charge is negligible.

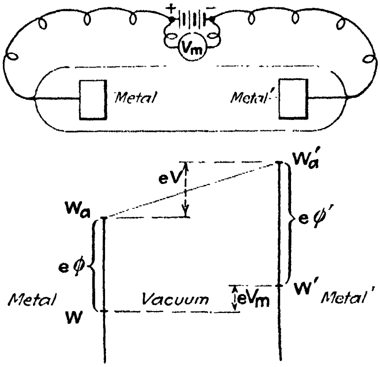

FIG. 6-4.—A diagram indicating the relative energy conditions of two electrodes, having different work functions, connected through a battery of potential V_m.

As we have seen before, the maximum energy of the electrons at 0° Abs. is W, and, as the temperature is raised, a certain number of them acquire energies in excess of this amount. If they are to reach the plate, this energy must be sufficient to carry them over the potential wall W_a at the surface of the metal, and in addition it must be great enough to permit them to surmount the hill eV between the surfaces of the filament and plate, due to the actual retarding potential V. We may therefore take over Eq. (6-7), which was developed for the case of no retarding field, by replacing the W_a that appears there by $W_a + eV$. We hence have as an expression for the thermionic current when a retarding potential V exists between the surfaces

$$
\begin{aligned}
I &= 2A_0T^2e^{\frac{-(W_a+eV-W)}{kT}} = 2A_0T^2e^{\frac{-(W_a-W)}{kT}}e^{-\frac{eV}{kT}} \\
&= 2A_0T^2e^{\frac{-e\phi}{kT}}e^{\frac{-eV}{kT}} = I_0e^{\frac{-eV}{kT}} \qquad (6\text{-}18)
\end{aligned}
$$

where I_0 is the saturation current of Eq. (6-8). It should be observed that here V is the potential difference between the surfaces, namely, the resultant of the applied potential V_m, as read with a meter, and the contact potential V_c. The energy conditions are as in Fig. 6-4; the contact potential may be either positive or negative. In carrying an electron from the metal of the filament over to the plate and back through a battery to the filament again, the total work must be zero (neglecting the Joule heating and the small Peltier effect where dissimilar metals are joined).

Hence

$$(W_a - W) + eV - (W_a' - W') - eV_m = 0$$

or

$$e\phi + eV - e\phi' - eV_m = 0$$

Hence

$$V = V_m + \phi' - \phi$$

or

$$V = V_m + V_c \tag{6-19}$$

Only in the case that the filament and plate are of the same material with the same surface conditions will the two potential walls be the same, *i.e.*, $e\phi = e\phi'$ or $V_c = 0$.

Equation (6-8) was developed for plane-parallel electrodes, strictly speaking, but since the potential barrier of the metal is so small in thickness compared to the diameter of the filament, the analysis holds equally well for cylindrical electrodes. This generality is not true for Eq. (6-18), however, since the retarding field extends all the way to the collecting plate. This radial field in the cylindrical case then has an appreciable influence on the other components of the electron's momentum, which were neglected before; a more extended analysis given by Schottky[1] shows that Eq. (6-18) must be altered for a thin wire filament surrounded by a cylindrical plate of large radius and may be approximately given as

$$I = I_0 \frac{2}{\sqrt{\pi}} \sqrt{\frac{eV}{kT}}\, e^{\frac{-eV}{kT}} \tag{6-20}$$

Taking the logarithms,

$$\log_{10} I = \text{constant} + \log_{10} \sqrt{\frac{eV}{kT}} - \frac{eV}{kT} \log_{10} e \tag{6-21}$$

since the saturation current is a constant for a given temperature. The term $\log_{10} \sqrt{eV/kT}$ is small compared to eV/kT and therefore may be considered approximately constant, so that a plot of log I against the retarding potential V should yield a straight line of slope $-0.4343e/kT$, if the potential is expressed in electrostatic units. From this slope the temperature of the filament may be computed and compared with that found experimentally by an optical pyrometer. It is found in practice that the curve is a straight line only over its lower portion, before the effects of space charge make themselves felt; at this point the curve begins to follow the $\frac{3}{2}$ power of the potential. This break in the curve becomes less and less distinct for higher temperatures where the emission is more copious. For low temperatures the break may be considered to occur at the point where no potential exists between the surfaces, so that comparison with the meter reading permits a determination of the contact potential between the filament and the collecting plate.

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[1] Schottky, *Ann. Physik*, **44**, 1011 (1914).

The validity of Eq. (6-20) has been very accurately verified, most recently by Germer,[1] and for a time was thought to supply evidence that the velocity distribution inside a metal was the classical one, for Eq. (6-20) can also be deduced on the classical statistics. We have seen, however, that the assumption of a Fermi-Dirac distribution leads to exactly the same equation, since only those electrons escape from the metal for which $\epsilon > W_a > W$, which permits dropping unity in comparison with $e^{\frac{-(W-\epsilon)}{kT}}$ as in Eq. (6-6); hence the Fermi-Dirac distribution inside the metal degenerates to the classical form for those electrons that do escape.

6-7. Experimental Verification of the Laws of Thermionic Emission.—Vacuum tubes that are commercially available are adequate to demonstrate the validity of the theoretical relation connecting the temperature of a body and the maximum thermionic current from it, as given by Eq. (6-8), and also to verify that the current, when limited by space charge, varies as the $\frac{3}{2}$ power of the applied potential, according to Eq. (6-16). To investigate the distribution of velocities of the emitted electrons, and to make an accurate measurement of e/m by the space-charge effect, it is necessary to use a specially designed tube.

Almost any of the usual two- or three-electrode vacuum tubes may be used to investigate the first two of these phenomena. In the case of three-electrode tubes, the plate and grid should be connected together, thus forming a single electrode in addition to the filament. Those tubes in which the filament is oxide coated, in order to obtain large emission at low temperatures, are slightly less satisfactory for the verification of Eq. (6-8) than are those with filaments of a pure metal. The specially prepared cathode surfaces are covered with an electropositive material whose work function is very low; as this appears in the numerator of the negative exponential term in Eq. (6-8), the current is proportionally large, but, due to the effect of electric fields on the emission from such surfaces, the saturation voltage is not well defined. Furthermore, if the potential applied to such cathodes and the current drawn from them are large, the surface is profoundly altered and sudden changes may occur in the work function. Hence when this type of filament is used, care must be taken not to apply too large a voltage or to draw too large a current; the manufacturer's ratings should not be exceeded. Untreated filaments are not restricted in this way and may also be used over a wider range of temperatures. Tubes in which the elements have cylindrical symmetry, with a filament whose radius is small in comparison with that of the plate, such as the General Electric magnetrons, are particularly convenient and may be used to obtain an approximate value of e/m from the space-charge equation.

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[1] GERMER, *Phys. Rev.*, **25**, 795 (1925).

The circuit is indicated in Fig. 6-5. The size of the batteries B_1 and B_2 depends upon the tube used; in order to cover the maximum temperature range, B_2 should be large enough so that the maximum safe anode current is not limited by space charge when the full potential of B_2 is applied. About 200 volts is generally sufficient. The filament battery B_1 may be replaced by a step-down transformer if desired. The filament should be shorted by a center-tapped resistance of about 100 ohms in order that the voltage read by the meter V may more nearly correspond to the potential difference between the center of the filament (where the temperature is highest) and the collecting electrode. It is generally necessary to apply a retarding potential between the plate and filament in order to bring the electron current completely to zero. This is due to the contact potential between the surfaces and to the distribution of velocities of the electrons as they leave the filament. (This latter effect is small.) To provide this reverse field, the wire from the plate is connected to a point several cells from the end of the battery B_2, as shown in the figure. If B_2 is replaced by a generator, a few cells may be placed in series with it to supply this retarding field. A reversing switch permits the voltmeter to read potentials of either sign. The true zero of potential between the surfaces may be taken as the voltmeter reading (positive or negative, as the case may be) at which the current is zero, and subsequent voltage readings are then reduced to this zero value. This simple procedure is only valid, however, for small currents; for large currents the voltmeter reading must be further corrected for the potential drop in the center-tapped resistance across the filament and for that in the milliammeter M of known resistance, by the application of Ohm's law. This latter meter should be one with variable shunts and capable of recording currents from 10^{-6} to 10^{-1} amp.

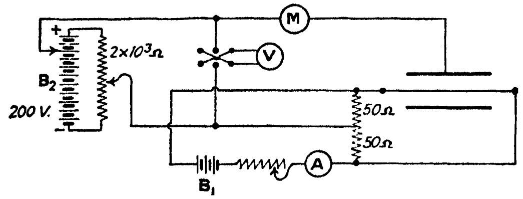

FIG. 6-5.—A circuit using a commercial vacuum tube to investigate the dependence of the saturation thermionic current on the temperature of the filament, and to demonstrate that the current when limited by space charge, below saturation, varies as the three-halves power of the accelerating potential.

When using commercial tubes the only method of measuring the filament temperature is by the use of an optical pyrometer. The principle of its operation depends on the radiation laws developed in Chap.

II. If we consider Eq. (2-35) for the wave lengths in the visible region, we see that the exponential term is very much larger than unity for all available temperatures. Hence we may write

$$E_\lambda \, d\lambda = c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T}} d\lambda \tag{6-22}$$

where $c_1 = 8\pi ch$ and $c_2 = hc/k$. This gives the relation between the effective energy emitted in a certain wave-length range by a black body and the temperature of the body. If, by some optical means, we compare the brightness of an incandescent-lamp filament with a black body when both are seen through a filter which transmits only a small wave-length range, we may vary the filament temperature by changing the current through it, until it is as bright as the black body. If the temperature of the latter is known, the critical current through the lamp may be identified with this temperature. In this manner a calibration curve may be obtained from a series of the black-body temperatures, and the temperature of any other black body may thus be found. A calibration curve for the particular lamp in each instrument is supplied by the manufacturer.

The filament in a vacuum tube is not a perfect black body, however, so that a correction factor must be introduced which depends on the emissive power of the filament. Let us assume that on matching the pyrometer lamp with the filament whose temperature is desired, we find the surface to have an apparent black-body temperature equal to τ; *i.e.*,

$$E_\lambda \, d\lambda = c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda \tau}} d\lambda \tag{6-23}$$

Since the surface is not perfectly black, it emits only a fraction e_λ of the energy in this wave-length region that a black body would radiate, where e_λ is the monochromatic emissive power. Therefore, in terms of the true temperature,

$$E_\lambda \, d\lambda = e_\lambda c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T}} d\lambda \tag{6-24}$$

Equating the right-hand sides of these two equations, and taking logarithms, we find

$$-\frac{c_2}{\lambda \tau} = \log_e e_\lambda - \frac{c_2}{\lambda T}$$

This may be solved for τ:

$$\tau = \frac{T}{1 - \dfrac{\lambda T}{c_2} \log_e e_\lambda} \tag{6-25}$$

From the measurements by Forsythe and Worthing[1] of e_λ for light of wave length 6650 Å (the usual color for optical pyrometer filters), we obtain the following table of the relation between the true temperature T and the apparent black-body temperature τ for a tungsten filament.

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[1] Forsythe and Worthing, *Astrophys. J.*, **61**, 146 (1925).

True Temperature T, Degrees Abs.	Apparent Black-body Temperature Degrees Abs.
1273	1217
1473	1397
1673	1575
1873	1749
2073	1921
2273	2089
2473	2255
2673	2418
2873	2575
3073	2733
3273	2887

As the emissive power varies but slightly with the wave length, these corrections to the pyrometer temperatures may be used for instruments calibrated anywhere within the color range from 6000 to 7000 Å. The emissive power decreases approximately 0.4 per cent for every thousand Ångströms increase in wave length.

In measuring the temperature of an object as small as a tungsten filament, it is generally most convenient to clamp the pyrometer to a stand. The distance to the filament does not affect the calibration, provided the filament is accurately focused by means of the objective lens on the calibrated filament of the pyrometer. The area of the image is approximately inversely proportional to the square of the distance of the object from the pyrometer, and, as the total radiation reaching the instrument is also inversely proportional to the square of this distance, the brightness of the image or the radiation per unit area is independent of the distance. If the vacuum tube to be used contains a "getter," a patch of the surface through which to see the filament may be cleaned by gentle heating with a Bunsen flame. If the getter cannot be entirely removed, a small error will be caused in the temperature measurement; an experimental test of the exponential form of Eq. (6-8) will not be invalidated, but the value found for the work function will not be correct.

Figure 6-6 indicates the current *vs.* potential curves at five temperatures obtained with a General Electric magnetron, type FH-11. Although designed as a short-wave oscillator, this tube may be used to advantage because of its symmetrical construction; the two semicylindrical plates are connected together to form a single anode. The curves for temperatures as low as 1800° Abs. are not shown because of the small ordinates they would exhibit on this scale. To show that the saturation currents for different temperatures obey Eq. (6-8), it is convenient to take the logarithm of that expression:

$$\log_{10} I - \log_{10} T^2 = \log_{10} \frac{I}{T^2} = \log_{10} 2A_0 - \frac{e\phi}{kT} \log_{10} e \qquad (6\text{-}26)$$

The variations in temperature are small compared with the corresponding changes in the current, so that the T factor on the left is practically constant compared to I. If we plot $\log_{10} (I/T^2)$ against $1/T$, we should obtain a straight line with a negative slope equal to $(e\phi \log_{10} e)/k$, or $(0.4343e\phi)/k$, or, if ϕ is expressed in volts, ϕ = slope/5,040. Figure 6-7 shows such a plot for the data of the preceding graph, including two additional points corresponding to the saturation currents at lower temperatures; the slope is 25,200, indicating a work function for the tungsten filament of ϕ = 5.0 volts. If we knew the area of the emitting

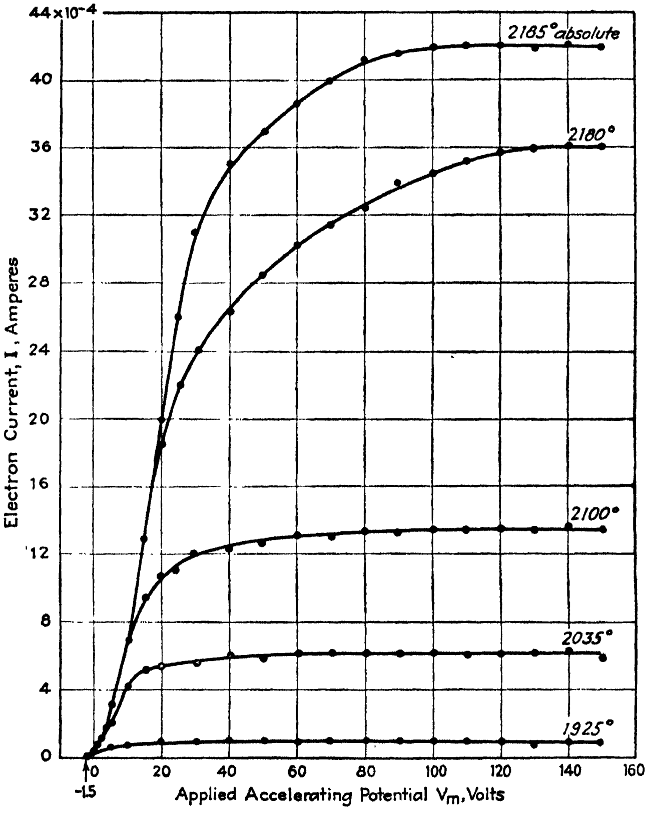

FIG. 6-6.—Curves showing the dependence of the thermionic current on the applied potential, at five different temperatures. A contact potential of 1.5 volts is indicated by the current not becoming zero until a retarding potential of this magnitude is applied.

surface, and if it were all at a uniform temperature, we could calculate the constant A_0 from the intercept on the ordinate.

To verify the dependence of the space-charge limited current on the $\frac{3}{2}$ power of the potential existing between the electrodes, we may take the logarithm of Eq. (6-16) and obtain

$$\log_{10} I = \log_{10}\left(\frac{2\sqrt{2}}{9b}\sqrt{\frac{e}{m}}\right) + \frac{3}{2}\log_{10} V \tag{6-27}$$

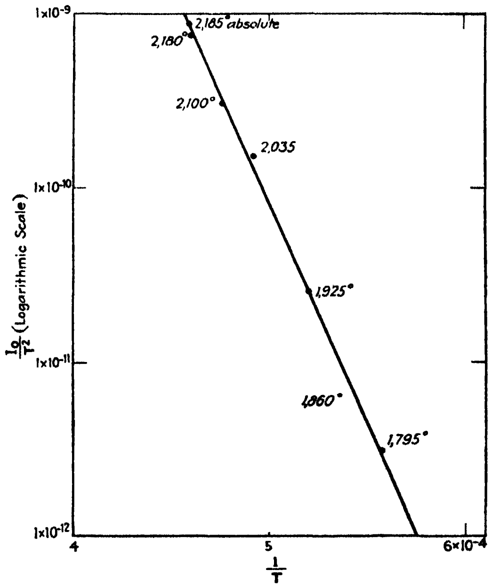

FIG. 6-7.—A graph indicating the validity of Richardson's law, Eq. (6-8), for the dependence of the saturation current on the temperature, through a plot of Eq. (6-26). The data are taken from Fig. 6-6 and include the saturation currents at two lower temperatures not shown in that figure.

Thus, if the logarithm of the current for any particular temperature is plotted against the logarithm of the potential between the surfaces, a straight line should result, with a slope equal to $\frac{3}{2}$. Figure 6-8 is such a graph for the 2185° curve of Fig. 6-6; the abscissas are the voltmeter readings plus the contact potential, as estimated from Fig. 6-6, where it is seen that the current drops to zero at about 1.5 volts applied retarding potential. The lower points of Fig. 6-8 are quite sentitive to a small change in the chosen value of the true zero of potential; this is less true for the points on the middle of the curve. The straight line has been drawn to have the slope $\frac{3}{2}$; departure from this line at the top indicates the condition when the saturation current is being approached. An approximate value of e/m may be found from any point on this curve; taking

$$I = 1.0 \times 10^{-4} \text{ amp.} = 3 \times 10^5 \text{ e.s.u.}$$

and the corresponding potential

$$V = 3.1 \text{ volts} = 1.33 \times 10^{-2} \text{ e.s.u.}$$

we obtain

$$\frac{I}{V^{\frac{3}{2}}} = 2.86 \times 10^{8}$$

Since the radius of the collector, b, is approximately 0.6 cm., we find by Eq. (6-16) that $e/m = 3.0 \times 10^{17}$ e.s.u. per gram or 1.0×10^{7} e.m.u. per gram. Better agreement with the correct value 1.761×10^{7} e.m.u. per gram cannot be expected; an appreciable fraction of the current is lost because the anode plates do not form a complete cylinder.

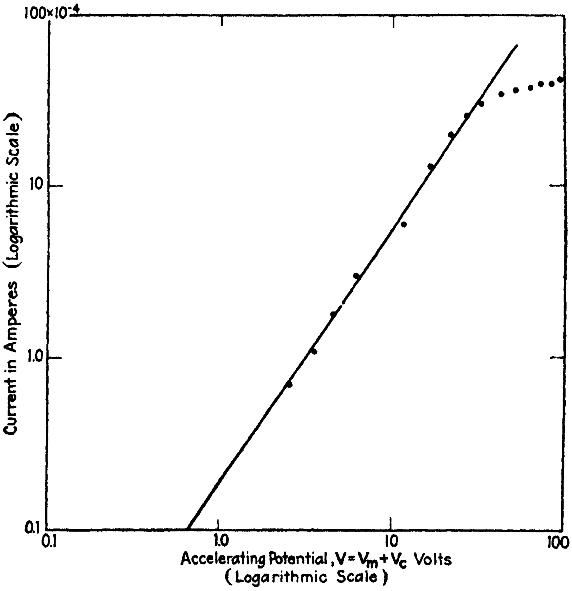

FIG. 6-8.—The variation of thermionic current, when limited by space charge, with the accelerating potential. The data of Fig. 6-6, for the 2185° curve, are here plotted according to Eq. (6-27), correction having been made for the contact potential. The straight line has been drawn to have the slope 3/2.

We shall now describe the construction of a tube suitable for the investigation of the distribution of velocities of the emitted electrons, for the determination of the constant A_0 and for a more accurate evaluation of the ratio e/m. The tube may also be used for the experiments previously described. The requirements are that there shall be cylindrical symmetry, with a filament of known area (small in diameter compared to the plate), and that electrons shall be collected only from a known length of the filament, of which this part must be at a uniform temperature. Figure 6-9 shows a tube designed to fulfill these conditions and also indicates the connections for measuring the velocity distribution

The anode is made of three coaxial cylinders of thin nickel sheet 12 or 15 mm. in diameter. The central portion may be about 1 cm. in length; the two outer cylinders are three or four times as long and are separated from the central section by not more than 1 or 2 mm. All three are kept at the same potential, but only the current to the middle cylinder is recorded. Here the cooling effect of the ends has little influence on the temperature of the filament. The outer cylinders act as guard rings and insure a purely radial electric field in the central region. The cylinders are supported by heavy nickel rods to which they are attached by short nickel strips, the joints being spot-welded. The lower ends of the rods are welded, or alternatively forced into holes in small nickel blocks, so that they may be fastened by means of set screws to the heavy tungsten leads passing through the glass pinch. It is convenient to form and align the cylinders by wrapping the nickel sheets around a wooden rod of the proper diameter, which is withdrawn after the electrodes are mounted. The filament is of tungsten wire about 5 mils in diameter

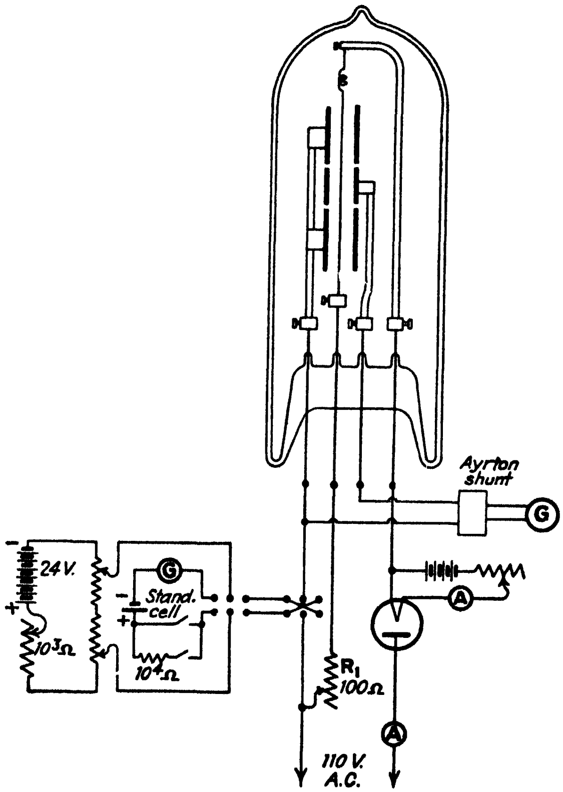

Fig. 6-9.—The details of construction of a tube and the wiring diagram suitable for investigating the distribution of velocities of thermionic electrons, for determining the magnitude of the constant A_0, and for evaluating the ratio e/m.

(0.005 in.); it is welded to short nickel rods which are engaged by set screws in a collar on one of the tungsten leads and in the nickel supporting rod. It is advisable to include a spring in the filament, to take up several millimeters of expansion when heated; this spring may be made by winding a few centimeters of 10-mil tungsten wire around a No. 40 drill. After assembling the electrodes, the glass press is sealed into a bulb and this in turn to the pumping system; a constriction should be made in the connecting tube if the bulb is to be sealed off. Details of the evacuating and baking technique are described in Appendix B.

When using this tube to verify Eqs. (6-8) and (6-16), the circuit is similar to that described for commercial tubes. The central cylinder is connected as if it were the plate of Fig. 6-5, the shunt box of a galvanometer replacing the milliammeter; the two guard cylinders are connected to the battery side of the shunt so that the only current measured is that to the middle electrode. Optical-pyrometer measurements of the temperature of the central part of the filament may be made through the space between the cylinders, or the temperature may be calculated by means of the tables given by Jones and Langmuir;[1] we give below an extract, showing the values of the function $A' = A/d^{\frac{3}{2}}$ for various values of the temperature, where A is the current in amperes flowing through an aged tungsten filament of diameter d cm. The values are true only for a filament in a good vacuum, and no correction has been made for the cooling effect of the ends. This error is quite small for the central part of a long filament.

Temp., ° Abs.	A' amp. cm.$^{-\frac{3}{2}}$	Temp., ° Abs.	A' amp. cm.$^{-\frac{3}{2}}$
293	0.0	2000	1022
300	3.727	2100	1119
400	24.67	2200	1217
500	47.62	2300	1319
600	75.25	2400	1422
700	108.2	2500	1526
800	148.0	2600	1632
900	193.1	2700	1741
1000	244.1	2800	1849
1100	301.0	2900	1961
1200	363.4	3000	2072
1300	430.9	3100	2187
1400	503.5	3200	2301
1500	580.6	3300	2418
1600	662.2	3400	2537
1700	747.3	3500	2657
1800	836.0	3600	2777
1900	927.4	3655	2838

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[1] JONES and LANGMUIR, *Gen. Elec. Rev.*, **30**, 310 (1927).

Since the diameter of the filament is known, and as the length of it which is emitting the recorded current is the same as the length of the central electrode, the emitting area can be computed, so that the constant A_0 may be found from values of the saturation current by the use of Eq. (6-8). Furthermore, since the geometrical conditions for which Eq. (6-16) is valid are quite accurately fulfilled, a more satisfactory value of e/m can be obtained.

The electrical connections for verifying the distribution of velocities through Eq. (6-18) are shown in Fig. 6-9. The potential between the filament and cylinder is applied by a potentiometer arrangement, such as a Leeds and Northrup type K, which is capable of supplying potentials up to 16 volts. A 24-volt battery supplies the driving current which creates the desired potential difference at the potentiometer terminals. This method of using a potentiometer is valid only if the current drawn is very much smaller than the current flowing in the potentiometer. As the thermionic currents are of the order of 10^{-10} to 10^{-6} amp., while that in the potentiometer is about 0.2 amp., the procedure is here quite permissible. The galvanometer used to measure the electron current to the collecting cylinder should have as high a current sensitivity as possible; an Ayrton shunt may be used to reduce the sensitivity and thus permit a wider range of current to be measured.

In order to avoid a spurious distribution of velocities due to a potential drop along the filament, it is necessary that no current be flowing through it when measurements of the thermionic emission are being made. This is accomplished by heating the filament with alternating current passed through a half-wave rectifier. When the plate of the rectifier tube is positive, so that the heating current flows through the filament, the potential drop in it and in the regulating rheostat R_1 is sufficient to keep the cylinders considerably negative with respect to the filament. Thus with 100 volts alternating-current supply, a filament current of 2 amp., and with the resistance of the filament and R_1 equal to 50 ohms, the retarding field is about 100 volts, which is ample to prevent any electrons from reaching the cylinders. During the other half of the cycle, when the plate of the rectifier tube is negative, no current flows through the filament, which is consequently at a uniform potential along its length. The region between the filament and the cylinders is then field free, except for whatever retarding potential may be applied by the potentiometer. The thermionic currents are measured and the filament heated during alternate half cycles by this arrangement. A rectifier capable of carrying 2 or 3 amp. should be used, such as a small hot cathode two- or three-element mercury-arc tube (General Electric phanotron.) If the frequency of the alternating current is high enough, the cooling of the filament between alternations is negligible. While 60 cycles can be used to give acceptable results, a small 500-cycle generator is more satisfactory.

If alternating current is not available, the filament may be heated with direct current interrupted by a commutator mounted on a motor shaft, which opens the heating circuit during half of each revolution. If the filament temperature is to be calculated from the heating current, its effective value may be read directly by an alternating-current ammeter included in the circuit. The procedure is to note the galvanometer current as the applied potential is varied in steps of, say, 0.2 volt, from 5 volts retarding to 5 volts accelerating. The result of such a run is indicated in Fig. 6-10 where $\log_{10} I$ is plotted against V_m, the potentiometer readings; the points lie fairly well on a straight line, as is predicted by Eq. (6-21). From the slope of the line, the characteristic temperature of the electron velocity distribution is calculated as 2420° Abs., while optical-pyrometer measurements indicate 2340°. This represents about the limit of error of the measurements. It is observed that the curve

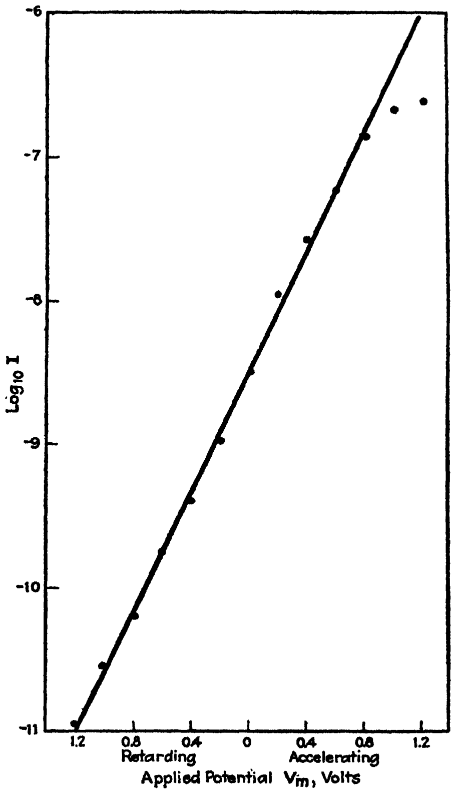

FIG. 6-10.—A plot of thermionic current against retarding potential to verify the velocity distribution among thermionic electrons as predicted by Eq. (6-21). An especially designed tube was used, as described in the text.

departs from a straight line at 0.8 volt applied accelerating potential; this point represents the true zero of potential between the filament and cylinder, indicating a retarding contact potential of 0.8 volt. With this and the value of the work function of the filament (obtained by an experiment with this tube such as yielded Fig. 6-6), the work function of the collecting cylinder can be computed through the use of Eq. (6-9).

6-8. Photoelectricity.—The discovery that a metallic surface, when illuminated by light of very short wave length, is able to emit electricity was made by Hertz in 1887,[1] during his fundamental researches in connection with an entirely different subject, namely, the resonance in electrical circuits. This discovery was investigated shortly afterward by Hallwachs[2] and by Elster and Geitel,[3] whose work established most of the fundamental phenomena of photoelectricity. As we have seen in an earlier chapter, Lenard and Thomson showed in 1898 that the ratio of the charge to the mass of the negatively charged particles emitted from a metal by the action of light had the same value as that for cathode rays. Hence the presumption that the particles were electrons was very strong, even at an early date. As the phenomena of photoelectricity are of such fundamental importance in physics, they have been the subject of careful investigation ever since their discovery. The enormous amount of experimental data which has accumulated and the modern interpretation have been presented by Hughes and DuBridge.[4]

The most important fundamental phenomena in connection with the ordinary surface photoelectric effect are the following:

1. If light of a given frequency is capable of liberating electrons from a surface, the electronic current is directly proportional to the intensity of the light.
2. For a given surface there is a longest wave length which can liberate electrons; light of longer wave length cannot free them, no matter how long it falls upon the surface or how great the intensity.
3. Light of wave length shorter than this critical value causes the emission of electrons, and the length of time which elapses between the illumination of the surface and the onset of the photoelectric current is not more than 3×10^{-9} sec.
4. The kinetic energy of the emitted electrons is directly proportional to the frequency of the light that frees them.

There are many other phenomena of great interest, such as the velocity distribution of the electrons, the effect of polarization and the angle of incidence of the light, the influence of the surface temperature and of applied electric fields, and the photoelectric behavior of thin films and composite surfaces. For a discussion of these points the reader is referred to Hughes and DuBridge.

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[1] Hertz, *Ann. Physik*, **31**, 983 (1887).

[2] Hallwachs, *Ann. Physik*, **33**, 301 (1888).

[3] Elster and Geitel, series of papers in *Ann. Physik* (1889–1892).

[4] Hughes and DuBridge, "Photoelectric Phenomena," McGraw-Hill (1932).

These phenomena represent some of the most important corroborations of the conclusions reached in Chap. II as to the inadequacy of the classical electromagnetic theory of light. From the old viewpoint it can be shown that it would take hours for an atom to absorb enough energy from an advancing wave train of visible light of moderate intensity to supply the energy with which the photoelectron is actually ejected, and yet experiment shows that the emission occurs almost instantaneously. Furthermore, the electromagnetic theory is entirely unable to account for the fact that the energy of the electrons is independent of the intensity of the light but depends only on the frequency. These facts, however, find ready explanation on the quantum or photon conception of radiation developed in Chap. II. No mechanism is supposed to exist for the gradual accumulation of energy by an atom; if the energy of the incident photon is less than some critical value, say, $e\phi$, for the particular surface under consideration, no electron is emitted, and if the energy is absorbed at all it must result in increased thermal motion. On the other hand, the assumption is made that if the photon has enough or more than enough energy, it is absorbed as a whole by one of the semifree electrons which then escapes, using a quantity $e\phi$ of the photon's energy $h\nu$ in getting free of the surface, and carrying away the excess in the form of kinetic energy. This radical viewpoint of energy interchange was propounded by Einstein[1] in 1905 and is embodied in his fundamental equation

$$h\nu = \frac{mv^2}{2} + e\phi \tag{6-28}$$

where on the left we have the energy of the photon and on the right the kinetic energy of the emitted electron and the work done by it in getting over the potential barrier of the crystal. (We may here use the nonrelativistic expression for the kinetic energy, since the velocities are small.) It should be noted that since $e\phi$ represents the work done against the forces holding the electron to the crystal, there must be an equal reaction against the crystal itself, which is thus the third body necessary for the complete disappearance of the photon and the ejection of an electron, as we have seen earlier in this chapter. The quantity $e\phi$ is the difference between the height of the potential wall, in energy units, and the maximum energy of the electrons within the crystal at 0° Abs. and hence should be identical with the work function defined in Eq. (6-8), where we were describing the thermionic effect, *i.e.*, $e\phi = W_a - W$.

The above equation is in accord with the experimental observation that the energy of the freed electron is proportional to the frequency of the radiation. An increase of photoelectric current with an increase of light intensity follows from the picture of greater intensity being due to an increased density of incident photons, assuming a constant value for the probability of absorption of a photon by an electron. (The efficiency of emission, or the number of electrons freed per incident photon, is generally very low; it varies with the surface and with the frequency. The highest photoelectric yield yet recorded is about one electron for every ten photons, but it may be as low as only one electron per million photons.) The Einstein equation may be tested by observing the "stopping potential" V_0, between the emitting surface and a collecting electrode, against which the electrons are just not able to advance. This means that the kinetic energy at emission is equal to eV_0, so we may write

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[1] EINSTEIN, *Ann. Physik*, **17**, 132 (1905); **20**, 199 (1906).

$$eV_0 = \frac{mv^2}{2} = h\nu - e\phi \qquad (6\text{-}29)$$

It is apparent that if the frequency of the light is reduced the kinetic energy becomes less, reaching zero at the threshold frequency ν_0, so that

$$h\nu_0 = e\phi \qquad (6\text{-}30)$$

A critical frequency ν_0 (or a critical wave length $\lambda_0 = c/\nu_0$) is thus predicted; lower frequencies should not cause any photoelectric emission at all. This is in agreement with the experimental facts. A plot of the stopping potentials for different frequencies against the latter should give a straight line of slope h/e, according to Eq. (6-29); the intersection with the voltage axis yields the value of ϕ, while the intercept on the ν-axis gives the threshold frequency ν_0. Studies of the photoelectric stopping potentials thus afford an extremely reliable method of determining Planck's constant h, if the electronic charge is assumed to be known. The most accurate values obtained by this method are given below.

Millikan,[1] 1916..............	$h = 6.57 \times 10^{-27}$ erg. sec.
Lukirsky and Prilezaev,[2] 1928.	6.543
Olpin,[3] 1930	6.541

The estimated errors in the last two values are about 0.1 per cent. These values are in excellent agreement with those obtained from the black-body radiation laws and from other types of experiment to be mentioned later.

If we have a tube suitably designed for measuring photoelectric currents from an illuminated surface against a retarding potential, the types of current-voltage curves that are obtained are similar to those in

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[1] MILLIKAN, *Phys. Rev.*, **7**, 355, (1916).

[2] LUKIRSKY, and PRILEZAEV, *Zeits. Physik*, **49**, 236 (1928).

[3] OLPIN, *Phys. Rev.*, **36**, 251 (1930).

Fig. 6-11. As the retarding voltage is decreased a photoelectric current sets in quite suddenly, the voltage at which this occurs depending on the wave length of the light used. As the retarding potential is further reduced, the current rises rapidly and reaches a saturation value which is attained at approximately the same voltage for all wave lengths. As the space charge is negligible for such small currents, it follows that at this potential all the electrons liberated by the surface at all wave lengths less than the critical value are able to reach the collecting plate. Hence this represents the true zero of potential difference between the electrode surfaces, and the variation between this and the apparent potential V_m, as read by a potentiometer, is the contact potential between the surfaces. In Fig. 6-11 the critical voltage is taken as that at which the curves first show a tendency to saturation; reflection of electrons at the collecting plate prevents the break from being ideally sharp. All the electron currents have been proportionally reduced to the same value at this point, since the absolute values of the currents are of little significance, as they depend on the intrinsic brilliancy of each color in the exciting mercury arc and on the transparency of the glass bulb of the cell for the different wave lengths. If the observed values of the stopping potentials, at which the currents first begin, are plotted against the frequency of the light,

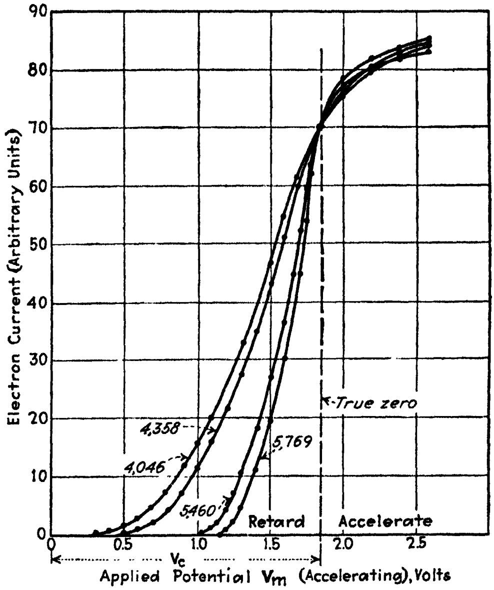

FIG. 6-11.—Photoelectric currents plotted against the applied potential, for several wave lengths of light. The ordinates have been proportionally reduced so that they all have the same value at the point where saturation sets in. This point locates the true zero of potential between the electrodes and indicates the magnitude of the contact potential V_c.

the points of Fig. 6-12 are obtained. They are seen to lie on a straight line in accordance with Einstein's relation, which may be written

$$V_m + V_c = V_0 = \frac{h\nu}{e} - \phi \tag{6-31}$$

where the true stopping potential V_0 is the algebraic sum of the potentiometer reading V_m and the contact potential V_c. The scale on the right of Fig. 6-12 represents the potentiometer readings, which are all 1.85 volts too large; *i.e.*, the contact potential is $V_c = -1.85$. The scale on the left shows the true stopping potentials when corrected by this amount. The intercepts indicate that the emitting surface has a long wave-length limit of 8815 Å ($\nu_0 = 34 \times 10^{13}$ sec.$^{-1}$) and a value of ϕ equal to 1.37 volts. By Eq. (6-9) we see that the contact potential is equal to the difference between the work functions of the emitting and collecting electrodes, so that the work function of the latter is 1.37 − (−1.85) or 3.22 volts. By means of Eq. (6-30) we see that this corresponds to a long wave-length limit of 3830 Å for the collector; the latter is therefore incapable of emitting any electrons under the influence of scattered light of the wave lengths used. This is an essential if the onset of photoelectric current is to occur abruptly. The ratio h/e is given by the slope of the line in Fig. 6-12, if the volts are divided by 300 to reduce them to electrostatic units, yielding the value 1.35×10^{-17}. Taking $e = 4.770 \times 10^{-10}$, we find $h = 6.44 \times 10^{-27}$ erg sec., which is within 2 per cent of the accepted value. It is obvious that any error in choosing the contact potential from the breaks in the curves of Fig. 6-11 will affect only the

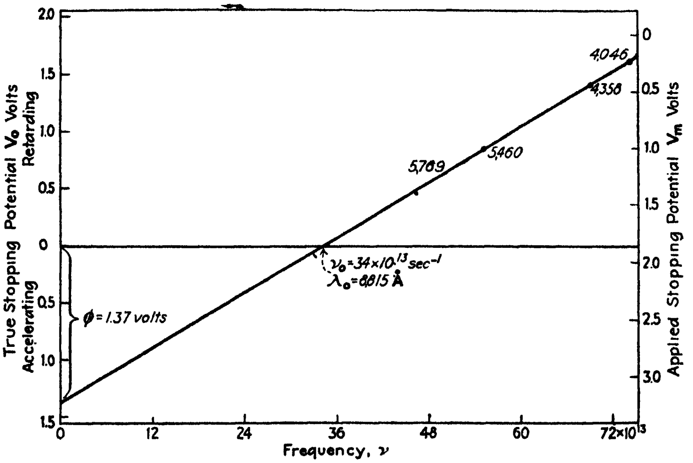

FIG. 6-12.—A plot of the data of Fig. 6-11 to demonstrate the validity of Einstein's equation for photoelectricity. Here the stopping potentials for the emitted electrons are plotted against the frequency of the light. The slope of the resulting straight line is equal to the ratio h/e.

values of the work functions and long wave-length limits, without influencing the determination of h.

The shape of the photoelectric current curves below saturation is of considerable interest. The general form of the energy distribution curve for electrons in a metal, as shown in Fig. 6-2, explains the sharpness with which the curves of Fig. 6-11 leave the axis. At 0° Abs. this angle should be unmistakably finite, since the electrons in the metal then have a sharply defined upper limit to their energy, which when augmented by the energy of the photon $h\nu$ must be equal to, or greater than, the height of the potential barrier W_a, if the electrons are to escape. At higher temperatures the onset of the photoelectric current becomes less abrupt, due to the rounding off of the energy distribution curve in the metal. The actual energy distribution of the electrons leaving the surface can be computed from the current-voltage curves below saturation if the emitter is small and at the center of a spherical collector, so that the total energy is measured and not merely the component normal to the surface as is the case with plane-parallel electrodes. An analysis by magnetic deflection can be used to calculate the energies directly. Such experimental energy distribution curves agree fairly well with that which would be predicted from the internal distribution curve, similar to Fig. 6-2, on the assumption (doubtless only a first approximation) that the probability of absorption of a photon by an electron is independent of the electron's original energy. If the latter quantity were simply increased by an amount $h\nu$, the energy distribution curve of Fig. 6-2 would merely be shifted to the right along the axis a distance $h\nu$, and the distribution of the electrons that escape would be given by the portion of the curve for which $W + h\nu$ is greater than the potential barrier W_a.

The saturation portion of the current-voltage curves exhibits many of the same characteristics as the analogous part of the thermionic diagrams. Strong fields effectively lower the work function. This is most marked in the case of composite surfaces. A factor influencing the photoelectric effect, that is not present in the case of currents from heated filaments, is the so-called *reverse emission*. Electrons may be released from the surface intended as the collector because of light scattered to it, unless its work function is sufficiently high to prevent this. Such emission has the result of lowering the curves of Fig. 6-11 in the region below saturation, and it introduces considerable uncertainty in the exact points of departure of the curves from the axis, with consequent error in the determination of the ratio h/e.

6-9. Experiments on Photoelectricity.—Verification of the linear relation between photoelectric current and intensity of illumination can be made with any ordinary photo cell. A tube with a composite surface, such as the Western Electric type 3-A is very satisfactory, as the currents are so large that a sensitive galvanometer may be used to record them.

The experimental set-up is indicated in Fig. 6-13. An Ayrton shunt and galvanometer are connected in series with the cell and a battery of from 20 to 50 volts. The illumination may be supplied by a 100-watt incandescent lamp, preferably with a frosted bulb, as the angular distribution of the emitted light is more uniform. With this arrangement the light intensity or energy density per unit area decreases as the square of the distance from the lamp. The galvanometer currents are recorded as the lamp is placed at various distances, D, from the cell, and a plot of the current against $1/D^2$ yields a straight line. In order to calculate, from the slope, the number of electrons liberated per photon falling on the surface, the source would have to be monochromatic and the energy radiated per second at that wave length would have to be known, as well as the transmission coefficient of the bulb of the photo cell.

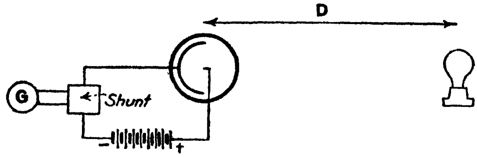

FIG. 6-13.—A diagrammatic sketch of an apparatus to demonstrate that the photoelectric current varies directly with the light intensity.

For an accurate evaluation of the ratio h/e a tube of special design must be employed, since the reverse emission from the collector in ordinary tubes prevents a reliable determination of the stopping potentials for various wave lengths. A photoelectric cell, such as has been described by Olpin,[1] has been used to obtain the data given in Figs. 6-11 and 6-12, through the courtesy of the Bell Telephone Laboratories. In order to eliminate reverse emission, the light-sensitive surface is deposited on the emitting electrode in the chamber B (see Fig. 6-14). This electrode is then allowed to slide down the glass rod inside the tube, until it is surrounded by the soot-covered nickel cylinder in chamber A. This cylinder acts as the collecting electrode. The work function of the sodium surface, activated with sulphur, is only 1.37 volts, so that light of wave length shorter than 8800 Å is capable of ejecting electrons from it. On the other hand, radiation of wave length greater than about 3800 Å cannot free electrons from the cylinder, because of its large work function of 3.22 volts. Hence, in the range from 3800 to 8800 Å, a photoelectric current can be caused only by the sodium surface.

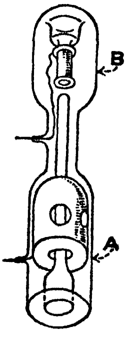

FIG. 6-14. The photoelectric cell, designed to eliminate reverse emission from the collector, used in the determination of h/e.

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[1] OLPIN, *Phys. Rev.*, **36**, 251 (1930).

The schematic arrangement for the use of this tube is shown in Fig. 6-15. The most convenient source of illumination is a small quartz or glass mercury arc. The mercury lines in the visible can be obtained with great intensity from such a source; if of quartz, the arc should be properly housed for protection of the operator from the strong ultra-violet radiation, which may cause serious burns. With an arc that runs on direct current, it is advisable to include a large inductance in the circuit, such as a transformer winding, to promote steadiness of operation. The adjustable resistance R_a limits the current to its rated value. If a mercury arc is not available, a powerful incandescent tungsten-filament lamp may be used; smaller photoelectric currents will be obtained, however, and a very accurate calibration of the monochromator is required.

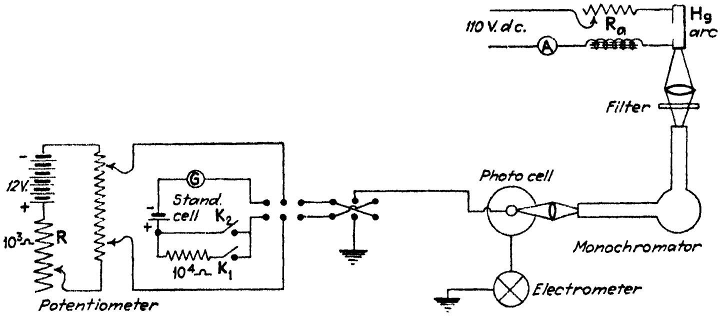

FIG. 6-15.—An arrangement for the photoelectric determination of the ratio h/e, by measurement of the stopping potentials for electrons liberated by different wave lengths.

The light is focused by means of a large condensing lens on the slit of a monochromator. A suitable instrument, where the highest accuracy is not essential, is a small constant-deviation spectroscope, which may be converted into a monochromator by replacing the eyepiece with a slit. In such an instrument there is inevitably a certain amount of scattered light not of the proper wave length reaching the exit slit, but as only light of shorter wave length is troublesome for photoelectric work, various filters may be inserted between the source and monochromator to cut out wave lengths shorter than that for which the instrument is adjusted. This is not absolutely essential, but the filters shown in the table on page 222 are suggested.

Two holes are provided in the collecting electrode of the photo cell, so that the light falling on the emitting surface through one opening may be observed through the other for adjustment. A small lens may be used to concentrate the light from the monochromator on to the surface. After adjusting the line up of the instruments by visual observation of the brilliant yellow or green lines, the fainter colors may be obtained with maximum intensity by looking into the exit slit of the monochromator with a small mirror while the dial is turned, or by adjusting this control near the approximately correct position until a maximum photoelectric current is obtained, with an accelerating field of 5 or 6 volts. The accuracy with which a particular spectral line may be isolated depends upon the dispersion of the monochromator; if the close groups in the table below cannot be separated, an error of about 0.5 per cent in the wave number will be introduced. Unless extreme care is used, this is generally within the other limits of error of the procedure described.

Line used		Filter	Short wave-length cut-off
λ	$\bar{\nu}$		
6,234.35 Å	16,035.8 cm.$^{-1}$	Wratten 29 or Corning 243	6,000 Å
6,123.47	16,326.1		
6,072.63	16,462.9		
5,790.66	17,264.5	Wratten 23	5,600
5,769.60	17,327.5		
5,460.74	18,307.5	Wratten 16	5,200
4,916.04	20,335.9	Corning 351	4,700
4,358.34	22,938.1	Corning Noviol A, 2 mm.	4,100
4,347.50	22,995.3		
4,339.23	23,039.1		
4,077.83	24,515.9	Corning 306	3,950
4,046.56	24,705.4		
3,662.88	27,293.2	Quinine sulphate in water. 3 mg./cm.^{3}. 10 mm., or	3,600
3,654.83	27,353.3	Corning 597, 3.2 mm. and 10 per cent CuSO$_4$ solution. 20 mm.	3,600
3,650.15	27,388.4		

The electrostatic shielding around the photo cell may conveniently be a thin galvanized-iron spouting 6 in. in diameter and 20 in. long; this acts also as a light shield. The upper and lower ends are fitted with light-tight caps, the photo cell being supported by a clamp passing through a hole in the upper one. The tubular metal shield around the lead wire from the collecting electrode to the electrometer enters through a hole in the spouting, and two other holes are cut in it for the admission of light and for observation. This latter opening may be covered with black paper when not in use; the light shield between the monochromator and the spouting may be a black-paper cylinder waxed into place. It is impossible to overemphasize the necessity of excluding from the photo cell absolutely all stray light, if satisfactory results are to be obtained. All the metal shields should be soldered together and thoroughly grounded; the wire from the emitting surface to the battery is insulated with cotton or rubber and may be passed through one of the end caps. For the intense light from a mercury arc, an ordinary Dolezalek electrometer used with the constant-deflection method is quite satisfactory, but for feebler sources a Compton electrometer or direct-current amplifying tube (such as the General Electric FP-54 pliotron) should be used. Details of technique may be found in Appendix A.

The retarding or accelerating potentials are supplied by a potentiometer and a reversing switch. The Leeds and Northrup type K is convenient, since it reads directly up to 16 volts, but the simpler type consisting merely of a set of calibrated resistances can also be used. If the normal range of the instrument is 1.6 volts, and if it is capable of maintaining its calibration for five times the normal current, potentials up to 8 volts can be obtained. The method of calibration for the higher range is simply to set the dials for one-fifth the voltage of the standard cell and to vary the external resistance R until the galvanometer shows no deflection when the keys K_1 and K_2 are closed in the usual manner. In this adjustment the actual potentials are five times the dial readings.

The method of procedure is to adjust the monochromator for the desired wave length and to reduce the retarding potential, in small steps, from a few volts to zero; then to throw the reversing switch and increase the accelerating field from zero to the potential at which saturation is reached. In the region where the photoelectric current is about to set in, the potential changes should be very small, about 0.05 volt; these critical regions may be found in a rough preliminary survey.

CHAPTER VII

LINE SPECTRA

7-1. Introduction.—Our study of atomic physics up to this point has dealt largely with the physical characteristics of material particles and radiation and to some extent with their interaction. The next two chapters will be concerned with the emission and absorption of radiation by atoms. A study of spectra leads to a theory of atomic systems as composed of elementary particles, namely a massive positively charged nucleus surrounded by an elaborate and complex structure of electrons. We shall be unable to pursue the theoretical developments to their recent culmination, but certain of the fundamental advances will indicate how the enormously involved mass of experimental data has been correlated into a consistent whole.

We shall confine ourselves to the study of the radiation from monatomic gases and vapors, the so-called *line spectrum*, in distinction to the radiation from a polyatomic gas which is known as a *band spectrum*. A great part of the light emerging from an incandescent gas such as hydrogen, nitrogen, or carbon dioxide is directly attributable to the molecular nature of these gases. The elementary particle, or molecule, of these substances is made up of two or more atoms of the element. Part of the spectrum gives us information as to the structure of the molecule and part as to the structure of the atoms composing it. With the exception of one section in the following chapter, we shall be concerned only with the radiation for which the atoms themselves are directly responsible. These two types of spectra may be distinguished by their different appearance on a photographic plate. An atomic spectrum is made up of a series of more or less sharp lines, whereas a molecular spectrum in general appears to be made up of a series of bands which are resolvable into separate lines only under very high dispersion. An adequate account of the most important characteristics of molecular spectra has been given by Ruark and Urey.[1]

We shall postpone the discussion of the theoretical developments through which the experimental facts are interpreted until we have made a brief résumé of the empirical spectroscopic knowledge up to the time of the concepts introduced by Bohr. The entire subject of line spectra is, of course, far too large to be dealt with adequately in this book. We shall have to content ourselves with an outline of the experimental facts and an indication of how they have been coordinated mathematically. For a thorough understanding of the subject the reader should acquaint himself with its early developments as given by Sommerfeld[1] or Andrade.[2] The standard works on the so-called vector model of the atom are those of Back and Landé,[3] and Hund.[4] The more recent theoretical developments of the subject are to be found in the accounts of Condon and Morse,[5] Pauling and Goudsmit,[6] and Sommerfeld,[7] and in the original papers. A complete bibliography of the experimental work from 1920 to 1931 has been given by Gibbs.[8] The symbolic notation used in spectroscopy has undergone many confusing variations; a table of the systems used by various authors has been given by Ruark and Urey.[9] Fortunately, as the theoretical interpretation of the phenomena has now become quite stable, a unified notation is coming into use. In this book we shall endeavor to keep consistently to the system which has been codified by Russell, Shenstone, and Turner.[10]

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[1] Ruark and Urey, "Atoms, Molecules, and Quanta," pp. 368*ff.*, McGraw-Hill (1930).

7-2. Early Empirical Spectroscopy.—When it is desired to obtain the spectrum of a given source, the light which it emits is concentrated upon a very narrow slit by means of a lens that is transparent to the region of the spectrum which is being observed or photographed. An image of this illuminated slit is formed by means of a series of lenses or concave mirrors upon a photographic plate, the images of the different colors corresponding to the different wave lengths being displaced sideways by the dispersion of a prism or grating. These images constitute the "lines" of the spectrum. A long narrow slit is used rather than an opening of any other shape for several reasons: the narrowness of the image permits the separation of colors only slightly different; extremely faint long images are easier to see than would be the images of a circular opening whose diameter equaled the slit width; it is easier to make a good slit than any other shape of adjustable diaphragm. The method of correlating the positions of these slit images with the wave lengths which they represent will be taken up in a subsequent section.

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[1] SOMMERFELD, "Atomic Structure and Spectral Lines," Methuen (1923).

[2] ANDRADE, "The Structure of the Atom," Bell (1930).

[3] BACK and LANDÉ, "Zeemaneffekt und Multiplettstruktur der Spektrallinien," Springer (1925).

[4] HUND, "Linienspektren und Periodisches System der Elemente," Springer (1927).

[5] CONDON and MORSE, "Quantum Mechanics," McGraw-Hill (1929).

[6] PAULING and GOUDSMIT, "The Structure of Line Spectra," McGraw-Hill (1930).

[7] SOMMERFELD, "Atombau und Spektrallinien," 5th ed., Vieweg, Braunschweig (1931).

[8] GIBBS, *Rev. Mod. Phys.*, **4**, 278 (1932).

[9] RUARK and UREY, "Atoms, Molecules, and Quanta," p. 297, McGraw-Hill (1930).

[10] RUSSELL, SHENSTONE, and TURNER, *Phys. Rev.*, **33**, 900 (1929).

From the earliest days of spectroscopy it was realized that the line spectrum given off by an incandescent vapor was characteristic of the vapor in question and to a certain extent of its temperature. The work of Bunsen and Kirchhoff brought the subject of spectrum analysis into prominence about 1859, and in the following years certain elements were actually discovered by this method. As the technique of measuring the wave length of light was improved, principally through the work of Fraunhofer, Ångström, and Rowland, interesting but baffling relationships between the characteristic lines of certain of the elements were noted. The presence of series of close pairs of lines in the spectra of the alkali metals was among the first of these interesting characteristics to be observed. It was also thought that certain numerical relationships had been found between the lines of the hydrogen spectrum, but these proved illusory. The first well-substantiated quantitative relation was discovered by Hartley,[1] who found that if frequencies were used instead of wave lengths, the frequency differences between the lines in certain recurring groups known as multiplets were the same for all similar multiplets occurring in the spectrum of the element. This was a very important observation and its significance will be seen when the empirical spectroscopic scheme is more fully developed.

Principally, however, attention was concentrated on the apparently simpler spectra such as those of hydrogen and the alkali metals. Certain series of lines were observed for these elements. From their similar behavior under various excitation conditions the members of these series, which were apparently single in the case of hydrogen and double in the cases of the alkalis, were evidently closely related to one another. The obvious method of attack was to search for numerical relationships between their wave lengths or frequencies. Contrary to the expectations of those pioneers in the study of spectra who were familiar with the properties of vibrating mechanical systems, neither the frequencies nor the wave lengths of the lines of a series could be made to fit any scheme of fundamental vibrations and their overtones or harmonics. A large amount of fruitless effort was expended in a search for these harmonic relations, which were expected by analogy with acoustical systems. The first successful representation of a series was achieved empirically by Balmer in 1885[2]. He showed that the lines in the visible spectrum of atomic hydrogen, as well as five lines in the ultra-violet (up to that time observed only in the spectra of the stars), could be represented very accurately by the equation

$$\lambda = 3{,}645.6\frac{n^2}{n^2 - 4}10^{-8}\text{ cm.} \tag{7-1}$$

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[1] HARTLEY, *J. Chem. Soc.*, **43**, 390 (1883).

[2] BALMER, *Ann. Physik*, **25**, 80 (1885).

where $n = 3, 4, 5, \cdots 11$. This discovery was the most fundamental step in advance which had been taken up to that time. However, due to its expression in terms of wave length rather than frequency, a great deal of its significance was not apparent. Balmer's success caused an abandonment of the search for harmonics and stimulated investigations for other series of a similar kind.

In 1890 Rydberg[1] discovered several of the most important characteristics of spectral series. He suggested formulating the expression for the series members in terms of the reciprocal of the wave length, *i.e.*, in terms of the wave number. Equation (7-1) then becomes

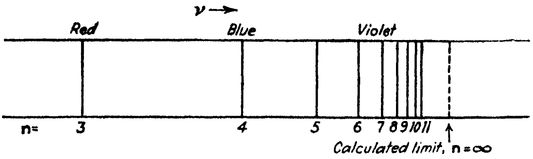

FIG. 7-1.—The Balmer series plotted on a frequency scale.

$$\begin{aligned} \tilde{\nu} &= \frac{1}{\lambda} = 27{,}430\left(1 - \frac{4}{n^2}\right) \\ &= R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \end{aligned} \tag{7-2}$$

where R is a constant, known as the Rydberg constant, whose value for hydrogen in accordance with the most modern measurements is $R = 109{,}677.759$ cm.$^{-1}$. This expression for the wave number of a line as the difference between two quantities, which bears a suggestive relation to the frequency differences observed by Hartley, was very important, but its significance was not fully realized at the time. Rydberg also recognized the existence of three series in the spectra of the alkali metals to which he gave the names *sharp*, *principal*, and *diffuse* as being somewhat characteristic of the different series. He further suggested that they could be approximately represented by an expression of the form

$$\tilde{\nu} = \tilde{\nu}_\infty - \frac{R}{(n + \mu)^2} \tag{7-3}$$

where n is a running number which takes successive integral values for the members of a series, μ is a small constant, and $\tilde{\nu}_\infty$ is the series limit, *i.e.*, the value of $\tilde{\nu}$ when n becomes infinite. This is only an approximation, and μ is not strictly constant, particularly for certain types of series. If μ is put equal to zero the expression reduces to the form of Eq. (7-2) which is thus included as a special type.

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[1] RYDBERG, *Kongl. Svenska Vet.-Akad. Hanglingar*, **23**, No. 11 (1890); *Phil. Mag.* **29**, 331 (1890).

Equation (7-3) may be written more symmetrically and in a way which brings out further possibilities as

$$\tilde{\nu} = R\left\{\frac{1}{(n_1 + \mu_1)^2} - \frac{1}{(n_2 + \mu_2)^2}\right\} \tag{7-4}$$

where $R/(n_1 + \mu_1)^2$ takes the place of $\tilde{\nu}_\infty$. Rydberg found that n_1 was generally unity, but he suggested that series might be found having different values of this constant. This idea was further developed by Ritz[1] who found that lines which would be predicted by taking differences between certain of the second terms of the Rydberg expressions [Eq. (7-3)] for different series were actually observed. Such differences are obviously of the form of Eq. (7-4). These observed lines were known as *combination lines*, and the principle of their prediction as *the combination principle*. To improve further the representation of series, many other forms of these terms whose differences represent lines were suggested. The only other type of equation for a term which we shall consider is that proposed by Ritz,[2] which contains an additional constant and also the term value itself in the denominator. This is capable of describing most series much more accurately than either the Balmer or Rydberg forms, but the process of series representation is more laborious, as there is the additional constant to determine. We may list the three types of *term formulas*, differences between which give the wave numbers of observed lines, as

$$\tilde{\nu} = \frac{R}{n^2} \qquad \text{(Balmer)}$$

$$\tilde{\nu} = \frac{R}{(n + \mu)^2} \qquad \text{(Rydberg)}$$

$$\tilde{\nu} = \frac{R}{(n + \mu + \alpha\tilde{\nu})^2} \qquad \text{(Ritz)}$$

It has been found that the lines in a spectrum such as that of sodium occur in close pairs. A double series is formed by pairs of lines having a constant wave-number difference between them; both the sharp and the diffuse series are of this type. On the other hand, the principal series is formed of double lines whose wave-number difference becomes continually less as the series limit is approached. There are certain interesting relationships between these series. The constant wave-number difference of the sharp and diffuse doublets is the same as that of the first doublet in the principal series, and the differences between the common limits of the sharp and diffuse series and the limit of the principal series are equal to the wave numbers of the lines of the first doublet of the principal series. These facts find a ready explanation in the Ritz combination principle and are most clearly brought out by the use of a *Grotrian*

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[1] Ritz, *Physik. Zeits.*, **9**, 521 (1908); *Astrophys. J.*, **28**, 237 (1908).

[2] Ritz, *Ann. Physik*, **12**, 264 (1903).

diagram, in which the values of the terms are plotted vertically, those terms that belong together in a family being plotted in separate columns for convenience. Such a column forms a series of terms and may be described by a formula such as the Rydberg or Ritz type. The number μ has a different value for each column; the P group of terms is double,

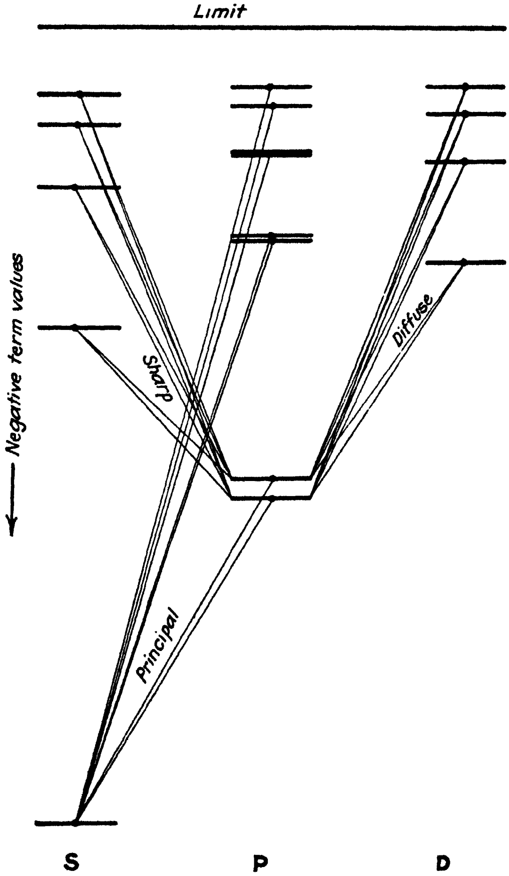

FIG. 7-2.—An example of a Grotrian diagram.

which may be described by giving μ two slightly different values. By the combination principle, the wave number of an observed spectral line is given by the difference between the values of two terms and is represented by a diagonal line connecting the terms involved. The principal doublet line series is then given by subtracting from the lowest S term the successive values of the double P terms, and it is apparent that these pairs of lines get closer together as the series limit is approached. On the other hand, the doublet sharp line series, obtained by subtracting from the lowest pair of P terms the successive S terms, is composed of pairs of lines of constant wave-number difference. A similar consideration applies to the double lines of the diffuse series, where the D terms are subtracted from the low pair of P terms. The origin of the other relationships that have been mentioned is easily understood from an inspection of the diagram.

Such a diagram can be constructed for any element, as it depends merely on the combination principle. For most other elements the series of terms are not double but show some other multiplicity. For example in the alkaline earths, mercury, etc., the terms are single and triple. For still other substances, many higher multiplicities, up to eight levels per term, are observed. It was found by Zeeman, as will be mentioned later, that if the light source is placed in a magnetic field, the lines of the spectrum are each separated into several very close components. This implies a splitting of certain terms in the diagram so that the complexity of the system is greatly increased. It is this enormous mass of empirical material represented by these plots for all the elements which must be accounted for by any satisfactory theory. We shall be able to indicate only a few of the simpler of these theoretical developments. For this purpose the Grotrian type of diagram will prove a very convenient basis for discussion. Its interpretation will be greatly enlarged and clarified through the theoretical significance which its terms receive.

7-3. The Atomic Theory of Bohr.—The experiments on photoelectricity, thermionics, and cathode rays had shown that electrons were a universal constituent of matter. The electromagnetic theory definitely stated that the acceleration of an electric charge must cause the emission of radiation. The obvious conclusion was that the atoms of each element contained electrons which could oscillate with certain frequencies and thus give off the spectrum characteristic of the element. The immediate stumbling block to such a theory was that this system of oscillators should exhibit the classical phenomena of harmonics, and these were not to be found, as has been mentioned before. Furthermore the experiments of Rutherford and Chadwick on the scattering of α particles by matter indicated that the positively charged part of the atom must be very small compared to the region occupied by the negative charge, whereas the oscillator type of atom suggested by Thomson required a large region of positive charge through which the electrons passed in order that their motion might be simple harmonic. If on the other hand the motion were circular and the radiation were caused by the continual acceleration toward the small nucleus demanded by Rutherford, we are faced with the difficulty that the light given off should form a continuous spectrum. The electron would spiral in faster and faster toward the nucleus, radiating away all its original potential energy until it eventually coalesced with the central positive charge. Thus the classical electromagnetic theory could provide no satisfactory structure for the atom. These difficulties were swept away and a satisfactory theory of the simple hydrogen atom was obtained at one grand stroke by Bohr.[1] This was done at the expense of violating the electrodynamic laws when convenient, accepting Planck's suggestion that radiation is emitted and absorbed only in discrete units, and by inventing an extremely arbitrary rule governing angular momentum.

Other series of lines besides that of Balmer are known for hydrogen. One was discovered by Lyman[2] in the ultra-violet, which can be represented by a formula similar to Eq. (7-2) but with $1/1^2$ as the first term in the bracket. Others have been found by Paschen,[3] Brackett,[4] and Pfund[5] in the infra-red, for which the first terms are of the forms $1/3^2$, $1/4^2$, and $1/5^2$, respectively. Thus we may write a general expression for all the atomic hydrogen series as follows:

$$\tilde{\nu} = R\left(\frac{1}{n'^2} - \frac{1}{n^2}\right) \tag{7-5}$$

where n' may have the values from 1 to 5, and n runs through a series of values beginning with $n' + 1$. It is to an expression of this form that any satisfactory theory of the hydrogen atom must lead. We may arrive at one such theory in a very simple manner as follows.

Imagine the nucleus to possess an infinite mass and a charge of $+e$ and that there is one electron with a mass m and a charge $-e$ which rotates around the nucleus in a circular orbit of radius r. Let us assume that it does not radiate any energy in spite of its central acceleration. If it is in equilibrium in the orbit, the centrifugal force mv^2/r is balanced by the electrostatic attraction e^2/r^2. We may write this condition as

$$\frac{mv^2}{r} = \frac{e^2}{r^2} \tag{7-6}$$

Hence the kinetic energy may be written as

$$T = \frac{mv^2}{2} = \frac{e^2}{2r}$$

The potential energy, which is taken as zero when r is infinite, is a negative quantity and may be written as $U = -e^2/r$. The total energy E, which is given by the sum of T and U, may thus be written as

$$E = -\frac{e^2}{2r}$$

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[1] Bohr, *Phil. Mag.*, **26**, 1, 476, 857 (1913).

[2] Lyman, *Astrophys. J.*, **23**, 181 (1906); **43**, 89 (1916).

[3] Paschen, *Ann. Physik*, **27**, 537 (1908).

[4] Brackett, *Astrophys. J.*, **56**, 154 (1922).

[5] Pfund, *J. Optical Soc. Am.*, **9**, 193 (1924).

Here we make the further assumption that only those orbits are possible for which the angular momentum is an integral multiple of the quantity $h/2\pi$, where h is Planck's constant. This is possible because h has the dimensions of either energy times time or momentum times distance. This so-called *quantization* of the angular momentum is a vital assumption of the theory. Thus

$$mvr = \frac{nh}{2\pi} \tag{7-7}$$

where n is an integer known as the total quantum number. Eliminating v between Eqs. (7-6) and (7-7) we obtain

$$r = \frac{n^2h^2}{4\pi^2me^2} \tag{7-8}$$

which gives us the radii of these possible orbits. Substituting this value of r in the expression for E, we obtain the possible values for the total energy in a "stationary state"

$$E = -\frac{2\pi^2me^4}{n^2h^2} \tag{7-9}$$

Now let us suppose that the electron suddenly changes to a smaller orbit characterized by the quantum number n'. Its energy in this new position is less than before (a larger negative quantity). Here we make the assumption, following the lead of Planck and Einstein, that the excess energy of the electron, over and above that needed for the new orbit, is radiated away as a quantum or photon whose frequency is proportional to its energy, the constant of proportionality being h. We are thus led to the fundamental Bohr frequency relation

$$h\nu = E - E' \tag{7-10}$$

Substituting the values of Eq. (7-9) in Eq. (7-10) we obtain

$$h\nu = \frac{2\pi^2me^4}{h^2}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$$

The frequency of the radiation is found by dividing both sides through by h, or the wave number by dividing by hc. Thus

$$\tilde{\nu} = \frac{2\pi^2me^4}{h^3c}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$$

$$\tilde{\nu} = R\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$$

This is of the same form as Eq. (7-5) which we wished to obtain, and the numerical value of the constant R is given by

$$R = \frac{2\pi^2me^4}{h^3c}$$

We thus see that these assumptions, which are largely due to Bohr, permit the derivation of a general expression for the entire spectrum emitted by atomic hydrogen. This is not surprising, however, in view of the revolutionary character of the assumptions made. The point that demands the greatest attention is the agreement, within about 0.1 per cent, of the empirical value of the constant R with that calculated from Bohr's equation when the values of e, m, h, and c are substituted in it. This constituted a great step forward in the understanding of atomic radiation. The conception of the transference from one orbit to another of an electron rotating about a nucleus, as the essence of the mechanism of radiation, formed the basis of most of the subsequent development of spectroscopic theory during the decade after its introduction. We may very briefly consider some of its further successes.

The preceding theory can be extended very simply to the case of other hydrogen-like atoms, *i.e.*, one-electron atoms such as singly ionized helium or doubly ionized lithium. It is merely necessary to represent the charge on the nucleus by Ze instead of by e, where Z is the atomic number of the element. The energy in a stationary state is then given by:

$$E = -\frac{2\pi^2 m Z^2 e^4}{n^2 h^2} = -\frac{Z^2 Rhc}{n^2}$$

The wave number of the emitted light is given by

$$\tilde{\nu} = RZ^2\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$$

This explains at once why some lines of the helium spectrum can be represented by the Balmer equation when it is multiplied by 4, which is a well-known experimental fact. If these lines are due to singly ionized helium, *i.e.*, helium atoms which have lost one of their two electrons, the emitting system is a nucleus with a charge $2e$ ($Z = 2$) with a single planetary electron revolving around it. This is electrically equivalent to a hydrogen atom with a double charge on the nucleus.

Let us now consider the effect of removing some of the simplifying assumptions which we introduced. In the first place let us assume that the mass of the nucleus is not infinite but is equal to M. We then know that the electron and nucleus rotate about the common center of gravity. If they are distant r and R, respectively, from the center of gravity, we have by definition: $mr = MR$. Multiplying this equation by the angular velocity of rotation ω, we have

$$mr\omega = MR\omega \text{ or } mv = MV$$

where v and V are the tangential velocities of the electron and nucleus, respectively. The total kinetic energy is given by

$$T = \frac{1}{2}mv^2 + \frac{1}{2}MV^2 = \frac{1}{2}mv^2\left(1 + \frac{m}{M}\right)$$

Since the separation of the nucleus and the electron is equal to $r + R$ which is $r + \frac{mr}{M}$, the potential energy, if the nucleus has a charge Ze, is given by

$$U = -\frac{Ze^2}{r\left(1 + \frac{m}{M}\right)}$$

The equations analogous to Eqs. (7-6), and (7-7) are then

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2\left(1 + \frac{m}{M}\right)^2} \tag{7-6'}$$

$$E = T + U = -\frac{Ze^2}{2r\left(1 + \frac{m}{M}\right)}$$

$$mvr + MVR = mvr\left(1 + \frac{m}{M}\right) = \frac{nh}{2\pi} \tag{7-7'}$$

These lead to the following equation for the total energy, E:

$$E = -\frac{2\pi^2 me^4Z^2}{n^2h^2\left(1 + \frac{m}{M}\right)} = -\frac{2\pi^2\mu e^4Z^2}{n^2h^2} = -\frac{Z^2Rhc}{n^2} \tag{7-9'}$$

where the so-called reduced mass μ and the Rydberg constant for the case of a nucleus with a finite mass are given by the relations

$$\mu = \frac{m}{1 + \frac{m}{M}} \quad \text{and} \quad R = \frac{2\pi^2\mu e^4}{h^3c}$$

We see from the above relations that the Rydberg constant depends on the mass of the particular nucleus with which we are concerned. The largest value that R can have theoretically is that obtained when M is infinite; we shall write this as R_∞. The value of the Rydberg constant for hydrogen is evidently given by

$$R_{\mathrm{H}} = \frac{R_\infty}{\left(1 + \frac{m}{M_{\mathrm{H}}}\right)}$$

and for singly ionized helium:

$$R_{\mathrm{He}} = \frac{R_\infty}{\left(1 + \frac{m}{M_{\mathrm{He}}}\right)}$$

Eliminating R_∞ from these two relations and solving for m/M_{H} we obtain:

$$\frac{m}{M_{\mathrm{H}}} = \frac{R_{\mathrm{He}} - R_{\mathrm{H}}}{R_{\mathrm{H}} - \frac{M_{\mathrm{H}}R_{\mathrm{He}}}{M_{\mathrm{He}}}}$$

From the atomic weights measured with a mass spectrograph or by chemical methods we know that the ratio of M_{He} to M_{H} is given by

$$\frac{M_{\text{He}}}{M_{\text{H}}} = \frac{4.0022}{1.00778} = 3.971$$

Experimental measurements of the Rydberg constants for hydrogen and helium, by methods which will be explained later, yield the following values:

$$R_{\text{H}} = 109{,}677.759 \pm 0.05 \text{ cm.}^{-1}$$
$$R_{\text{He}} = 109{,}722.403 \pm 0.05 \text{ cm.}^{-1}$$

whence we see that

$$\frac{M_{\text{H}}}{m} = 1{,}837.8$$

This agrees to within 0.5 per cent with the value 1,846 found from deflection measurements of e/m and e/M_{H} in Chap. IV. This is a very reassuring result. Since R approaches R_∞ very rapidly, the value R_∞ may be used with a negligible error for all but the very lightest elements. The value of R_∞ calculated from the experimental values of R_{H} and R_{He} is

$$R_\infty = 109{,}737.42 \pm 0.06 \text{ cm.}^{-1}$$

Largely in the hands of Sommerfeld, the Bohr atom was developed in more general terms. The possibility of elliptic orbits was dealt with by introducing the general quantum condition:

$$\oint p\,dq = \tau h$$

for each coordinate necessary to specify the position of the electron. Here p is the momentum or angular momentum associated with the coordinate q, τ is an integer known as the quantum number, and the integration is over a complete cycle of the variable. For a circular orbit, q is the angle θ through which the radius vector turns, and p is equal to mvr. Since the angular momentum is constant in a central force field, the integral of $mvr\,d\theta$ over a complete cycle is equal to $2\pi mvr$, and this formulation of the quantum conditions gives us the same result as Bohr's treatment of a circular orbit. Sommerfeld applied this condition to the momentum associated with both of the variables necessary to specify an ellipse, *i.e.*, the radius r and the angle θ. This introduces two quantum numbers; the azimuthal quantum number k and the radial quantum number n_r. The resultant expression for the energy of an elliptical orbit is found to be

$$E = -\frac{2\pi^2\mu e^4 Z^2}{(n_r + k)^2} = -\frac{Z^2Rhc}{(n_r + k)^2} \tag{7-11}$$

It is seen that this gives the same value for the energy as in the case of a circular orbit for which the total quantum number n is the sum of n_r and k. Since a knowledge of the energy levels of an atom does not suffice to distinguish between the various possible electron orbits which have the same value of $n_r + k$, we may consider that we have a number of elliptical orbits and one circular one coalescing to give only one term. Such a situation received the appellation "degenerate." Sommerfeld also showed that if the relativistic variation of mass with velocity were taken into account for the electron the degeneracy would be removed, and each particular combination of n_r and k would give rise to a different term. This would give each line of the spectrum a fine structure, *i.e.*, each line would in reality be two or more lines very close together. This is actually found to be the case for hydrogen, and the term separations found experimentally agree very well with those predicted by Sommerfeld.

Equation (7-11) bears a striking resemblance to the empirical expression of Rydberg, but there is an important difference. Here the denominator is the sum of two integers, whereas in a Rydberg term it is an integer plus a small quantity which is in general a fraction. A qualitative explanation of how the denominator of Eq. (7-11) may not be an integer can be obtained in the following way. For elements other than hydrogen the nucleus is surrounded by several electrons. These will disturb the electric field of the nucleus, and the electron responsible for the emitted light will no longer be moving in the Coulomb field of a point charge. It has been shown by Sommerfeld[1] that if the field is derivable from a potential function of the form

$$U = -\frac{Ze^2}{r} + \left(\alpha_0 + \frac{\alpha_1}{r} + \frac{\alpha_2}{r^2} + \cdots\right)$$

where the expression in brackets represents the non-Coulomb nature of the field, the terms are given to a first approximation by the Balmer form, to a second approximation by that of Rydberg, and to a third approximation by that of Ritz. The quantity in the bracket of the term denominator can be considered as an effective quantum number n^*. The difference between this and the corresponding hydrogen quantum number n, which for a Ritz term is of the form

$$n^* - n = \mu + \alpha\bar{\nu}$$

is known as the *quantum defect* and is a measure of the non-Coulomb nature of the field. This was a very great success for the older form of the quantum theory, but the quantitative agreement between the empirical constants of a Ritz term and reasonable values of the α's, which represent perturbing terms on the Coulomb field, was much less satisfactory.

While these early developments provided merely the opening wedge for the theoretical treatment of spectra from the point of view of the electron structure of an atom, they introduced certain fundamental conceptions. The most important of these was the identification of spectroscopic terms with the energy levels of an atom. Upon this idea the Grotrian diagram is immediately interpretable as a plot of atomic energy states through the Bohr frequency relation. The direct experimental verification of this important point will be taken up in the following chapter. The quantitative success of these early developments stopped with the simple hydrogen or ionized helium atom, *i.e.*, with an atom which contains only one electron in addition to the nucleus. Its success in those cases and its partially satisfactory description of certain other simple atomic phenomena led to the feeling that these ideas were qualitatively correct. This conception of an atom may be briefly summarized as a heavy nucleus surrounded by an external electron structure, the configuration of which can be specified by certain parameters known as quantum numbers; the atoms emit radiation of the frequency given by the Bohr relation when the internal energy determined by this configuration decreases from one allowed value to another.

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[1] SOMMERFELD, "Atomic Structure and Spectral Lines," Appendix 13, Methuen (1923).

7-4. The Vector Model.—The first grasp of the general principles underlying the description of spectra came from the work of Catalan[1] on the highly complex multiplets of the manganese spectrum rather than from the simple spectra which might at first sight have been considered to afford better possibilities for the observation of broad generalities. Next in importance was the introduction by Russell and Saunders[2] of the conception of spectral terms as properties of the atom or of the electron configuration as a whole rather than of a single radiating electron. This was followed very shortly by the theoretical developments due to Pauli,[3] Goudsmit,[4] Heisenberg,[5] Hund,[6] and Uhlenbeck and Goudsmit[7] which led to the purely empirical but very complete descriptive scheme known as the vector model. Inasmuch as this body of principles ties together the spectra of all the elements and lends a particular significance to the quantum numbers in terms of which the energy levels are described, we shall briefly state its more important postulates and their consequences. It is to be regarded as a set of empirical rules the interpretation of which, in terms of the more physical conception of electrons in an atomic system, is to be arrived at only through a study of the quantum mechanical theory of complex spectra. Such a study is far beyond the scope of this treatment, though the elementary consideration of the simple hydrogen atom will be outlined in a subsequent section.

For the purposes of the vector model we require the following postulates and definitions:

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[1] Catalan, *Phil. Trans.*, **223**, 127 (1922).

[2] Russell and Saunders, *Astrophys. J.*, **61**, 38 (1925).

[3] Pauli, *Zeits. Physik*, **31**, 765 (1925).

[4] Goudsmit, *Zeits. Physik*, **32**, 794 (1925).

[5] Heisenberg, *Zeits. Physik*, **32**, 841 (1925).

[6] Hund, *Zeits. Physik*, **33**, 345, 855 (1925); **34**, 296 (1925).

[7] Uhlenbeck and Goudsmit, *Physica*, **5**, 266 (1925); *Nature*, **117**, 264 (1926).

1. Each electron has associated with it an integral quantity n, known as the total quantum number by analogy with the similar quantity used by Bohr and Sommerfeld in the description of simple spectra.

2. Each electron has also a quantity l, sometimes known as the orbital quantum number, associated with it which fulfills the condition $l \leqslant n - 1$. This is closely connected with the angular momentum of an electron in a Bohr orbit on the older conception. The actual value of the angular momentum is equal to $lh/2\pi$. l is a vector quantity, and its values of 0, 1, 2, 3, 4, etc., are represented by saying that the electron is of the type *s*, *p*, *d*, *f*, *g*, etc., respectively, in analogy with the nomenclature sharp, principal, and diffuse of the series which have been described previously.

3. Each electron has associated with it another vector quantity represented by s. It is also of the nature of an angular momentum which for the purpose of concreteness may be thought of as a rotation or spin of the electron about its axis. It has, however, certain very remarkable properties, into which we shall not be able to go, that differentiate it from ordinary mechanical angular momenta. The value of s is $\frac{1}{2}$ for all electrons and the actual value of the angular momentum associated with s, which is $sh/2\pi$, is therefore $h/4\pi$.

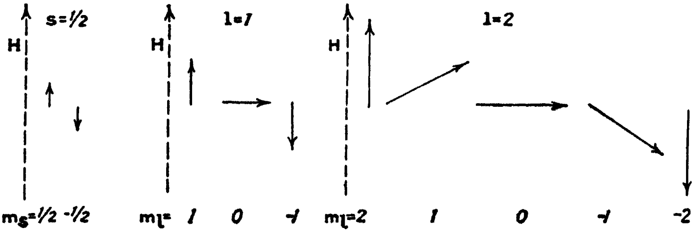

FIG. 7-3.—An illustration of the space quantization of vectors.

4. The total angular momentum quantum number of an electron, which is the vector sum of l and s, is written as j. It has half integral values only, these being $l \pm s$.

5. In an extremely large magnetic field these vector quantities would orient themselves in such a way that the projections of the l's and s's along the field would be integers or half integers, respectively. Thus these projections, which are known as magnetic quantum numbers, are given by

$$-l \leqslant m_l \leqslant l \text{ and } -s \leqslant m_s \leqslant s$$

m_l may have the $2l + 1$ values from $-l$ to l, and m_s may have the two values of $\pm\frac{1}{2}$.

The mechanism of interaction of the electrons in an atom, known as coupling, determines the characteristics of the configuration as a whole and hence of the spectrum terms or energy levels. If the principal influence is exerted between the separate l's and s's of the individual electrons, we may consider that the vectors represented by these different letters add up vectorially to give L and S vectors of the configuration or of the atom as a whole.

$$L = \sum_i l_i \text{ and } S = \sum_i s_i$$

We thus have a series of L values, depending on the orientation of the l's, designated by S, P, D, etc., respectively, characteristic of the different term series which in the Grotrian diagram are represented by the columns. The vector sum of L and S, which is the total angular momentum vector of the atom J, is also quantized; *i.e.*, it has only half integral values if S is a half integer or integral values if S is an integer. Its value is generally written as a subscript of the letter designating the L value. These vectors L, S, and J specify the terms due to the electron configuration. This type of electron interaction is known as Russell-Saunders or L-S coupling. All other types are possible, to the opposite extreme where the l and s vectors of each individual electron combine to yield j values whose sum is the atomic J value; we need only consider L-S coupling for the spectra to be described later.

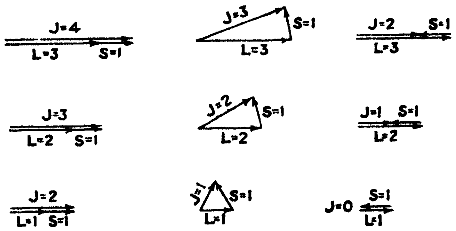

FIG. 7-4.—Illustrations of the additions of the quantum numbers L and S to form the resultant J.

To consider the possible structure or configuration for a given number of electrons surrounding a nucleus with a large positive charge we need the fundamental *restriction principle*, due to Pauli: that for no two electrons in any one atom may the corresponding four quantum numbers be the same. If we consider the atom in an extremely large magnetic field, we may choose as our four quantum numbers, say for the ith electron:

n_i = total quantum number
l_i = orbital angular momentum quantum number
m_{l_i} = component of l_i along the field
m_{s_i} = component of s_i along the field

Let us assume for the moment that the electrons occupy the lowest possible energy levels in the normal state and that these are the levels for which n is smallest. Then if we have but one electron in an atom its

n value is 1. Of necessity its l and m_l values are zero and its m_s value may be $\pm\frac{1}{2}$. There is thus room for one other electron of this n value for which $m_s = \mp\frac{1}{2}$. If there are more than two electrons one must have an n of 2; for this one there are two possibilities for l, namely 0 or 1. In the former case, as for the first electron, there are two possibilities for m_s namely $m_s = \pm\frac{1}{2}$; but in the latter case, as m_l may have the values -1, 0, and 1, for each of which we have the possibilities of $\pm\frac{1}{2}$ for m_s, we have six different combinations. This process can be continued for any number of electrons with increasing values of n to give us the largest number of a given type specified by n and l present in an atomic system. The electrons of a given n value are frequently said to compose or occupy a shell. These are known as K, L, M, etc., shells in X-ray nomenclature corresponding to the values of $n = 1, 2, 3$, etc., respectively. When all the possible combinations of the quantum numbers l, m_l, and m_s for a given n represent electrons actually present, the shell is said to be closed. The total number of electrons of any particular type for a given n is evidently equal to the number of possibilities for m_l times the number of possibilities for m_s. As the former is $2l + 1$ and the latter is 2 the total number is $4l + 2$. The following table may be constructed for the number of electrons of each type possible in the various closed shells.

NUMBER OF ELECTRONS

n	Type s	Type p	Type d	Type f
1	2			
2	2	6		
3	2	6	10	
4	2	6	10	14

A closed shell has a very important property as may be seen from the following array representing six p electrons:

$$\begin{array}{lcccccc} m_l = & 1 & 1 & 0 & 0 & -1 & -1 \\ m_s = & \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \end{array}$$

The sums of the quantities in each of these rows are equal to zero, therefore the resultant L, S, and J for the configuration as a whole are also all zero. As a consequence, if another electron were added to the atom, the resultant L, S, and J values of the atom (the sums of the respective values for the closed shell and those of the new electron) would be simply those of this electron. As these are the quantum numbers which specify the spectroscopic terms, we see that they are determined only by the last electron and that the effect of the closed group may be neglected. Similarly if we took any one of the electrons out of the above array, the possible values of the resultant Σm_l would be 1, 0, and -1 and those of

Σm_s would be $+\frac{1}{2}$ and $-\frac{1}{2}$, which corresponds to an $L = 1$ and an $S = \frac{1}{2}$, characteristic of a single p electron. In general the presence of any number of electrons, say x, in a closed group gives rise to the same terms as a number of electrons, y, of the same type, where $x + y$ is the total number possible in the group. The systematic development of these ideas yields a beautifully regular and complete skeleton framework of the types of terms to be expected for every possible electron configuration. For the details of these calculations reference should be made to the treatises on spectroscopy which have been cited. We shall consider briefly only those types of terms to be expected in the case of a one-electron spectrum, *i.e.*, one electron besides a closed group, and in the case of a particularly simple type of two-electron spectrum as represented by mercury.

If we have one electron outside a closed group it can have any total quantum number n greater than that of the closed group of its type. It can have an l value of 0, 1, 2, 3, etc., corresponding to its being of an s, p, d, f, etc., type; as this determines the L of the atom, the spectral terms will be S, P, D, F, etc., respectively. As the s of an electron is $\frac{1}{2}$, the S of the atom has also this value;* and the J, which is the vector sum of L and S, can have the values $L = 0$, $J = \frac{1}{2}$; $L = 1$, $J = \frac{1}{2}$ or $\frac{3}{2}$; $L = 2$, $J = \frac{3}{2}$ or $\frac{5}{2}$, etc. As there are two J values associated with each L (except $L = 0$), the spectrum is known as a doublet spectrum, as is signified by writing an anterior superscript 2 before the letter designating the L value of the term. The terms to be expected are thus:

$${}^2S_{\frac{1}{2}} \quad \text{or} \quad {}^2P_{\frac{1}{2}} \quad \text{and} \quad {}^2P_{\frac{3}{2}} \quad \text{or} \quad {}^2D_{\frac{3}{2}} \quad \text{and} \quad {}^2D_{\frac{5}{2}}, \text{ etc.}$$

There will be a level of each type (up to $L = n - 1$) for each n value the electron, and these series for increasing values of n represent the series of terms in the columns of the Grotrian diagram. Reference to the sodium spectrum later in the chapter will bring out clearly the application of this nomenclature to the diagram.

The other case we need consider is a simple two-electron spectrum for which one electron is of an s type, *i.e.*, $l_1 = 0$. In this case the L of the atom is the l of the second electron, as $L = l_1 + l_2$ and $l_1 = 0$. The S value, which is the vector sum of s_1 and s_2, both of which are $\frac{1}{2}$, can have the values 0 or 1. When $S = 0$, $J = L$; and when $S = 1$, $J = L + 1$, L, or $L - 1$. For $S = 0$ we have single terms, *i.e.*, only one J value; while for $S = 1$ we have triple terms, *i.e.*, three J values per term (except when $L = 0$). In general, as can be seen from the above example, the multiplicity of a spectrum is $2S + 1$. The terms to be expected from such electron structures are thus

$${}^1S_0,\ {}^3S_1 \text{ from } ns\ n's;\ {}^1P_1,\ {}^3P_{2,1,0} \text{ from } ns\ n'p;$$

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* In this sentence s and S refer to the spin of the electron and atom respectively. The small s used here must not be confused with the symbol meaning $l = 0$.

$^1D_2$, $^3D_{3,2,1}$ from $ns\ n'd$; etc.

where the letters S, P, D, etc., correspond to the s, p, d, etc., of the second electron, and the series of terms of a similar type are due to increasing total quantum numbers of this electron. The application of this nomenclature to a Grotrian diagram can be seen from that of mercury later in the chapter.

Working backward in our description of the vector model we come to the final experimental test, namely the comparison of the combinations between these terms and the observed spectrum lines. For this purpose, since all possible intercombinations are not observed, we find that we need the following principles restricting the configuration changes:

The L Selection Rule.—Only those combinations occur for which the sum of the l vectors of the electrons forming the initial and final states of the atom changes from an even to an odd number, or *vice versa.* Even terms are often written as S, P', D, F', G, etc., and odd terms as S', P, D', F, G', etc. Recently a more logical notation has come into use: odd terms are denoted by S^0, P^0, D^0, etc. and even terms by S, P, D, etc. In simple spectra where no confusion can result, such indices are usually omitted. For atomic states that are due to a single electron outside a closed group or an s electron and one other, as in the last example, this rule degenerates practically into the statement that the L value of the atom may change only by 1 or -1.

The J Selection Rule.—Only those combinations occur for which the J value of the atom changes by 1, 0, or -1, the transition of $J = 0$ to $J = 0$ being further excluded.

With these rules we find that even the most complex spectra become comprehensible. The application of them to the explanation of the observed lines of sodium and mercury will be described later. The complete designation of a line is given as the difference between the two terms of the final and initial configurations. If in the case of one electron it was originally of type p with a total quantum number of 4, the J of the atom being $\frac{3}{2}$ (term $4p\ ^2P_{\frac{3}{2}}$), and after the emission of radiation it became an s type of total quantum number 3 (term $3s\ ^2S_{\frac{1}{2}}$), the line would be completely represented by $3s\ ^2S_{\frac{1}{2}} - 4p\ ^2P_{\frac{3}{2}}$. Similarly if, in the case of the simple two-electron configuration, the original state of the atom was $6s9p\ ^3P_2$ and the final state $6s7s\ ^3S_1$, the line emitted would be written as $6s7s\ ^3S_1 - 6s9p\ ^3P_2$. When both electrons have the same n value a superscript is used, *i.e.*, $6s6s$ is written as $6s^2$.

For these simple types of electron structure the identification of lines and assignment of terms are relatively easy, but for complex spectra it is very difficult and tedious. Spectrum analysis consists in discovering the numerical values of the energy levels, transitions between which give rise to the observed lines. The actual process is very much like doing a cross-word puzzle backward; instead of being given the horizontal and vertical clues from which to derive the words, one is in effect given the words, which must first be set in their proper arrangement from which the clues are then to be deduced. Given the wave numbers of the observed radiation, the problem is to arrange sets of other numbers such that the differences between pairs of them correspond to the original data. The process is entirely one of trial and error, with certain rules for guides. If levels A and B both combine with C to give lines of wave numbers $C - A$ and $C - B$, then the wave-number difference between these two lines is equal to $(C - A) - (C - B) = B - A$. If there is another level D that also combines with the levels A and B forming the lines $D - A$ and $D - B$, the wave-number difference of these two lines is also $B - A$. Hence the list of wave numbers must be searched through for pairs of lines that have the same wave-number difference; the differences thus found determine the energies of the levels relative to an arbitrary zero taken at one of them. If a series of levels can be found that obey a Balmer, Rydberg, or Ritz formula, an absolute zero may be taken at the limit of the series of levels, *i.e.*, at the ion formed by the removal of an electron. This, however, is not necessary; relative energy levels may be used just as well as absolute ones, since only differences are important. The work is hampered by the fact that no wave-number measurements can ever be made exactly; a certain tolerance must be allowed when looking for constant differences. This leads to a large list of possibilities which can only be cut down to the true levels by cross differences and the aid of Zeeman patterns and certain empirical spectroscopic rules. Atomic radiations cover a vast range of wave lengths, and the experimental difficulties are very great except in the visible, near ultra-violet and near infra-red, so that in most cases only a portion of all the evidence for the construction of an energy-level diagram is at hand.

7-5. Quantum Mechanical Atom Model.—The highly empirical set of rules and principles embodied in the vector model has received a very complete and satisfactory theoretical justification through the application of quantum mechanics to the theory of complex spectra. These remarkable advances, which may be found in the work of Wigner,[1] Weyl,[2] Slater,[3] and others, lie far beyond our scope, but we may briefly consider the application of wave mechanical conceptions to the simplest possible atomic system, namely that of the hydrogen atom. As we shall see, the results of this theory are the same as those of the original Bohr theory based on an orbital electron. The success of quantum mechanics, however, in accounting for the experimental facts extends throughout the entire range of complex spectra, whereas the old semiclassical ideas were limited to the very simplest atomic systems.

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[1] Wigner, "Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren," Vieweg, Braunschweig (1931).

[2] Weyl, "The Theory of Groups and Quantum Mechanics," Methuen (1931).

[3] Slater, *Phys. Rev.*, **34**, 1293 (1929).

The fundamental equation which is to describe the behavior of the electron is Eq. (5-9) with the reduced mass μ replacing the mass of the electron in that equation:

$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}(E - U)\psi = 0 \tag{7-12}$$

It will be recalled that E is the total energy, U the potential energy, and ψ is the Schrödinger function whose absolute magnitude in a small region is to be taken as giving the probability of the electron being observed in that region. The symbol ∇^2 stands for the Laplace operator $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. In this discussion we shall not be interested in the solutions of Eq. (7-12) themselves but only in the necessary conditions that must be imposed on E in order that these solutions shall be finite, continuous, and single valued throughout space, which are necessary conditions if the solutions are to be acceptable for the description of an electron. For a hydrogen-like atom the potential energy U is given by $-Ze^2/r$, where Ze is the nuclear charge. In the case of hydrogen itself Z is, of course, unity. As this term is spherically symmetrical, it is more convenient to write the Laplace operator in polar coordinates and Eq. (7-12) becomes

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{8\pi^2\mu}{h^2}\left(E+\frac{Ze^2}{r}\right)\psi = 0 \tag{7-13}$$

We shall now assume that a solution of this equation may be written as the product of two factors, one a function of r only and one a function of θ and ϕ only:

$$\psi(r, \theta, \phi) = S(r) \times Y(\theta, \phi)$$

Substituting this in Eq. (7-13) we find that the equation groups itself into terms that depend only on r and terms that depend only on θ and ϕ. As the variables r, θ, and ϕ are independent and as the equation is to be true for all values of these variables, each of these groups of terms must be equal to a constant; if the first group is equal to $-C$, the second group must be equal to $+C$. We thus have two equations:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dS}{dr}\right) - \frac{C}{r^2}S + \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{r}\right)S = 0 \tag{7-14}$$

$$\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + CY = 0 \tag{7-15}$$

The second of these is familiar among mathematicians and the solution is well known. The point of extreme interest is that the solution is finite and continuous only if the quantity C has one of the series of values given by the relation

$$C = l(l + 1)$$

where $l = 0, 1, 2, 3, 4,$ *etc.*

We thus have an integral quantum number entering the picture quite naturally. It enters as the necessary consequence of the highly reasonable conditions which have been imposed on the solutions of the differential equation. This, of course, is much more satisfactory than the artificial introduction of this quantity in the older form of the quantum theory. The l defined above is the so-called orbital angular momentum of the vector model.

We may now put this value of C in Eq. (7-14) and make an attempt to solve it. The equation simplifies considerably if we define a new independent variable x and a new parameter n by means of the relations

$$E = \frac{2\pi^2\mu e^4 Z^2}{n^2h^2}$$

and

$$r = \frac{nh^2}{8\pi^2\mu e^2 Z}x$$

Equation (7-14) then becomes

$$\frac{d^2S}{dx^2} + \frac{2}{x}\frac{dS}{dx} + \left\{\pm\frac{1}{4} + \frac{n}{x} - \frac{l(l + 1)}{x^2}\right\}S = 0 \qquad (7\text{-}16)$$

A satisfactory solution of this equation may be found in the form of a polynomial provided that when E is negative, the parameter n is an integer and satisfies the relationship

$$n \geq l + 1$$

Thus the total quantum number of the vector model has also appeared quite naturally in the endeavor to solve these differential equations. The above transformation involving E and n is recognized as Bohr's expression for the energy of an electron in a circular orbit so that the allowed energy states agree with those of the Bohr theory for hydrogen. This is very satisfactory as we have seen that the energy states on the Bohr theory agree with those found experimentally in the case of hydrogen. The negative value of E is consistent with the convention that the zero of energy is taken at ionization, the various excited states and the normal state having negative energies. A solution of Eq. (7-16) is possible for a continuous range of values of n, if E is positive. This means that the energy content of the nucleus and electron can have any value when the atom is ionized; when the electron has sufficient energy to leave the atom it may fly off with any amount of kinetic energy.

This formulation of quantum mechanics not only supplies us with quantum numbers, but it also produces the selection rules governing the allowed transitions between atomic energy levels in a quite analogous manner, *i.e.*, as a result of the necessary properties of various mathematical expressions.

More complicated atoms than hydrogen do not admit of a simple solution of the Schrödinger equation [Eq. (7-12)] and so-called perturbation methods have to be used. The method is quite analogous in principle to that used in astronomy when the many-body problem is solved by successive approximations. Accounts of these methods are to be found in Ruark and Urey,[1] and Condon and Morse.[2]

As has been mentioned before, the solutions of even the simplest problems are often far from easy, involving the numerical evaluation of very formidable polynomials. It must be remembered, however, that these difficulties are probably only temporary, for when the useful expressions have been found they may be evaluated once and for all in tabular form. The infinite polynomial:

$$x + \frac{x^3}{3} + \frac{2x^5}{15} + \frac{17x^7}{315} + \frac{62x^9}{2{,}835} + \cdots \qquad \left(x^2 < \frac{\pi^2}{4}\right)$$

may give one pause until it is recognized by the abbreviation "tan x." It is to be hoped that analogous polynomials which occur in the solutions of problems in quantum mechanics will eventually become as familiar as the trigonometric functions.

7-6. The Normal Zeeman Effect.—Faraday, in 1862, endeavored to detect the effect of a magnetic field on light by placing a sodium flame between the poles of a magnet and looking for some change in the characteristic lines as seen through a spectroscope. He observed no alteration, but merely because of the relative crudity of his instruments. Zeeman,[3] in 1897, with better apparatus, succeeded in detecting a splitting of each spectral line into several components which had both longer and shorter wave lengths than the original line. This Lorentz explained in terms of the classical electromagnetic theory by showing how the frequency of an oscillating electron should be affected by a magnetic field. We shall here give, first, a simple quantum-theory explanation of the normal or simple Zeeman effect, wherein, when the light is observed in a direction normal to the field, each line becomes accompanied by two companions, one of higher frequency and one of lower frequency, the frequency differences between these and the original line being equal.

If an electron is revolving in an orbit about the nucleus and a magnetic field is applied, the electron is acted on by a force perpendicular both to the direction of the field and to the direction of the velocity vector at that instant so that the orbit becomes distorted. Its energy is changed so we may expect some alteration in the frequency of the light that is emitted when the electron performs a quantum jump to some other distorted orbit. It is sufficient for our purposes merely to write down the equations of motion of a particle of mass m_0 and charge $-e$ e.m.u. that is placed in a magnetic field of strength H directed along the Z-axis; we do not have to integrate and find the actual path. If the components of the atomic forces on the electron may be written as F_x, F_y, and F_z, we have by Eqs. (4-1), (4-2) and (4-3):

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[1] Ruark and Urey, "Atoms, Molecules, and Quanta," p. 551, McGraw-Hill (1930).

[2] Condon and Morse "Quantum Mechanics," Chap. IV, McGraw-Hill (1929).

[3] Zeeman, *Phil. Mag.*, **43**, 226 (1897).

$$\begin{aligned} m_0\ddot{x} - e\dot{y}H &= F_x \\ m_0\ddot{y} + e\dot{x}H &= F_y \\ m_0\ddot{z} \qquad &= F_z \end{aligned} \tag{7-17}$$

wherein we have used the abbreviations

$$\frac{d^2x}{dt^2} = \ddot{x},\ \frac{dx}{dt} = \dot{x}, \text{ etc.}$$

We shall now make use of a device due to Larmor. Let us find the equation describing the acceleration of a particle in a fixed frame of reference OX' OY' from the point of view of a coordinate system OX OY that is revolving with a uniform angular velocity $\dot{\psi}$ about the common OZ-axis of the two systems. The instantaneous y' coordinate, at the instant when the angular separation of the two systems is ψ, of a particle at x, y in the rotating system is then given by:

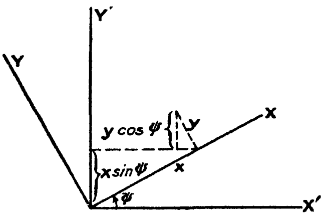

FIG. 7-5.—The transformation from a fixed to a rotating coordinate system.

$$y' = y \cos\psi + x \sin\psi$$

Hence, differentiating this with respect to the time

$$\dot{y}' = \dot{y}\cos\psi - \dot{\psi}y\sin\psi + \dot{x}\sin\psi + \dot{\psi}x\cos\psi$$

and differentiating a second time, remembering that $\dot{\psi}$ is a constant,

$$\ddot{y}' = \ddot{y}\cos\psi - 2\dot{\psi}\dot{y}\sin\psi - \dot{\psi}^2 y\cos\psi + \ddot{x}\sin\psi + 2\dot{\psi}\dot{x}\cos\psi - \dot{\psi}^2 x\sin\psi$$

Now, since $\ddot{y}'$ is the true acceleration along the direction Y', we can find the true acceleration along OX and OY by the use of the above expression at the instants when OY' lies along OX and OY, respectively. Thus when $\psi = \pi/2$

$$\text{Acceleration along } OX = \ddot{x} - x\dot{\psi}^2 - 2\dot{y}\dot{\psi}$$

and when $\psi = 0$

$$\text{Acceleration along } OY = \ddot{y} - y\dot{\psi}^2 + 2\dot{x}\dot{\psi}$$

So if F_x, F_y, and F_z are any external forces applied to a particle of mass m_0, the equations of motion in terms of the rotating axes are

$$\begin{aligned} m_0\ddot{x} - m_0 x\dot{\psi}^2 - m_0 2\dot{y}\dot{\psi} &= F_x \\ m_0\ddot{y} - m_0 y\dot{\psi}^2 + m_0 2\dot{x}\dot{\psi} &= F_y \\ m_0\ddot{z} &= F_z \end{aligned}$$

Comparing these equations with those representing the motion in a magnetic field, Eq. (7-17), we see that they are the same if we omit terms in $\dot{\psi}^2$, which are small, and if we identify $e\dot{y}H$ with $m_0 2\dot{y}\dot{\psi}$, and $e\dot{x}H$ with $m_0 2\dot{x}\dot{\psi}$, both of which give the relations,

$$\text{Angular velocity } \dot{\psi} = \frac{eH}{2m_0}$$

$$\text{Angular frequency } o = \frac{\dot{\psi}}{2\pi} = \frac{eH}{4\pi m_0}$$

The fact that these two sets of equations have exactly the same form to this approximation shows that the actual complicated path of the electron may be described by saying that the original orbit maintains its shape, but that the whole coordinate system by which it is specified rotates uniformly about the direction of the magnetic field with the angular frequency o, known as the Larmor precession frequency. The application of this to the Zeeman effect is quite simple. The kinetic energy of any system of electrons, each of mass m_0, is given in polar coordinates by

$$E_0 = \tfrac{1}{2}\Sigma m_0(\dot{r}^2 + r^2\dot{\theta}^2 + r^2 \sin^2\theta\dot{\phi}^2) \tag{7-18}$$

When we apply a magnetic field H along the Z-axis, the energy is given by the same expression provided we consider that the entire system rotates about OZ with the angular velocity $\dot{\psi}$. Hence in that case we have

$$E_H = \tfrac{1}{2}\Sigma m_0[\dot{r}^2 + r^2\dot{\theta}^2 + r^2 \sin^2\theta(\dot{\phi} + \dot{\psi})^2] \tag{7-19}$$

Expanding the bracket $(\dot{\phi} + \dot{\psi})^2$ and neglecting terms in $\dot{\psi}^2$, as we have done before, we obtain on subtracting Eq. (7-18) from Eq. (7-19)

$$\begin{aligned} \Delta E = E_H - E_0 &= \Sigma m_0 r^2 \sin^2\theta\,\dot{\phi}\,\dot{\psi} \\ &= \dot{\psi}\Sigma m_0 r \sin\theta\,(r \sin\theta\,\dot{\phi}) \\ &= 2\pi o p \cos(pH) \end{aligned} \tag{7-20}$$

where p is the total angular momentum of the atom and $\cos(pH)$ is the cosine of the angle between p and the field, so $p \cos(pH)$ is the projection of the angular momentum vector in the direction of H. Thus the increase in energy of the atom in a magnetic field is proportional to o, which is itself proportional to the field, and to the projection of the angular momentum along the field.

Let us first consider the case of one electron with the restriction that the $L - S$ coupling is much stronger than the couplings of either l or s with the field H. The angular momentum vector J is the sum of L and S, or expressed in the proper units it is $Jh/2\pi = p$. We now recall that the projections of the vectors along the magnetic field are quantized, *i.e.*, they have integral or half-integral values, hence the projection of J along the field, which is equal to $p \cos (pH)$ of Eq. (7-20), and which we shall write as M, can have only integral or half-integral values. Thus

$$\Delta E = Moh \quad \text{or} \quad E_H = E_0 + Moh \tag{7-21}$$

Any other electron level will undergo a similar increase in energy, so in a jump from one level to another an atom emits radiation of frequency ν given by

$$h\nu = (E_0 + Moh) - (E_0' + M'oh) = (E_0 - E_0') + (M - M')oh$$

or

$$\nu = \nu_0 + o\Delta M$$

where ν_0 is the frequency of the light emitted by transitions between the undisturbed levels, and ΔM is the change in the so-called magnetic quantum number M. The selection rule governing the change is $\Delta M = 1, 0, -1$. Hence for such an atom in a magnetic field the frequencies emitted are either

$$\nu_0, \; \nu_0 + o, \quad \text{or} \quad \nu_0 - o$$

In any actual light source there are a large number of atoms each of which may emit any one of the above frequencies, so these three frequencies are observed from the source. In the expressions for these frequencies:

$$o = \frac{eH}{4\pi m_0} = 1.397 \times 10^6 H \text{ sec.}^{-1} \text{ frequency units}$$

or

$$\frac{o}{c} = 4.674 \times 10^{-5} H \text{ cm.}^{-1} \text{ wave-number units}$$

where H and e are in electromagnetic units. Zeeman patterns are generally described in terms of the separation for a field of 1 gauss, *i.e.*, 4.674×10^{-5} cm.$^{-1}$. This is called the Lorentz separation. We therefore see that the above analysis predicts the splitting of a spectral line into three components: one at the original frequency, and one on either side at a distance, in wave numbers, equal to one Lorentz unit for a unit field strength. Measurements of the Zeeman effect therefore give an accurate value of the ratio of the charge to the mass of an electron in an atomic system. References to such experiments have been given in Chap. IV.

7-7. The Anomalous Zeeman Effect.—Although the above theory adequately describes the Zeeman effect for lines due to combinations between singlet terms, it is insufficient for the majority of other lines which are observed to split into more than three components when apparatus of sufficient resolving power is used. Such behavior was called "anomalous" when it was first observed, but as frequently happens the anomalous case turns out to be the general one, and the so-called normal case which we have just discussed is a very special instance. It has been found that the general

Zeeman effects can be described consistently if the increase in energy due to a magnetic field is written as

$$\Delta E = gMoh$$

instead of $\Delta E = Moh$ as in Eq. (7-21). The symbol g is known as the Landé g factor or splitting number. The special case which we have considered previously arises when $g = 1$. The significance of this factor may be most clearly brought out by the consideration of the energy of a small magnet of moment μ, which represents the atom when it is in a magnetic field H with the direction of its magnetic moment at an angle θ with the field. The potential energy is equal to $-\mu H \cos \theta$, as may be seen by integrating the torque $\mu H \sin \theta$, from $\pi/2$ to θ (the zero energy state being taken when $\theta = \pi/2$). Therefore, when a magnetic field of strength H is applied, the increase in energy may be thought of as this increase in potential energy:

$$\Delta E = -\mu H \cos \theta$$

If we consider that the magnetic moment is in the same direction as the angular momentum (as the moving charges are negative the opposite sign is used), and equate these last two expressions, writing $p \cos \theta$ from M, and $eH/4\pi m_0$ for o, we obtain

$$gp \cos \theta \frac{eH}{4\pi m_0} h = \mu H \cos \theta$$

from which we see that

$$g = \frac{\mu}{p}$$

if μ' is measured in units of $eh/4\pi m_0$. Thus the factor g is the ratio of the magnetic, moment to the angular momentum when the former is measured in units of $eh/4\pi m_0$, known as the *Bohr magneton*, and the latter in units of $h/2\pi$.

Let us now consider what value of g we should expect on the basis of classical electrodynamics for an electron, without any spin vector, traveling in a circular orbit. By elementary electromagnetic theory, the magnetic moment associated with a current of strength i flowing around the circumference of a circle of area A is given by $\mu = iA$, where i and μ are in electromagnetic units. Hence $\mu = ef\pi r^2$, where e is the electron's charge in electromagnetic units, f is the frequency of revolution in the orbit, and r is the radius of the orbit. For the orbital angular momentum we have $p_l = m_0 vr$, or $p_l = m_0 r^2 2\pi f$. Hence we find that the ratio of the magnetic moment, due to the orbital motion, to the orbital angular momentum is

$$g_l = \frac{\mu}{p_l} = \frac{ef\pi r^2}{m_0 r^2 2\pi f} = \frac{e}{2m_0}$$

If we express μ and p_l in their respective units, which we have previously adopted

$$g_l = 1$$

This means that the value of g associated with the orbital motion of an electron is 1, and this may be shown to be true for much more general cases than the one we have chosen.

Unfortunately the effect of the spin vector cannot be calculated in this simple way. In the previous discussion we have made the assumption, which is necessary to account for the observed spectroscopic phenomena, that the angular momentum associated with the electron spin is $sh/2\pi$, where s is always equal to $\frac{1}{2}$. In order to account for the general phenomena of the Zeeman effect, as well as certain allied phenomena such as the Stern-Gerlach effect and the so-called gyromagnetic anomaly, it is necessary to assume that the magnetic moment associated with the spin of an electron is $eh/4\pi m_0$, which is one unit of magnetic moment. This hypothesis, that in the case of this quantity, which we have called the electron spin, we have a whole unit of magnetic moment associated with only half a unit of angular momentum, gives effectively

$$g_s = 2$$

This is as radical a departure from the classical quantities of electrodynamics as were Bohr's postulates when they were first enunciated, and it can be justified only by the results which it yields. It has, in fact, permitted the construction of an adequate theory of magnetic phenomena.

We shall not go through these calculations, however, which can be performed accurately only on the basis of quantum mechanics, but shall simply state the resulting value of g for the atom as a whole, provided it exhibits Russell-Saunders coupling. This expression had previously been discovered empirically by Landé.[1]

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Tables of these g numbers for different values of L, S, and J are given by Back and Landé,[2] Ruark and Urey,[3] Pauling and Goudsmit,[4] and Hund.[5]

In a magnetic field we have seen that J is quantized; it can take only those orientations in the field such that its projection along the field, which we have called M, is integral or half integral according as J is integral or half integral. We have further seen that the increase in the energy of the atom because of the field is $\Delta E = Mgoh$, or taking oh as a unit, the increase in energy is Mg. The magnetic quantum number M may have any of the $2J + 1$ values $J, J - 1, J - 2, \cdots -(J - 1), -J$, or, as there are actually many atoms present in the light source, all the $2J + 1$ values of M may be considered to be present simultaneously. Now let us suppose that an atom changes from the state wherein $J = J_1$ and $g = g_1$ to the state $J = J_2$ and $g = g_2$. The effect of the magnetic field is to split each original J level into $2J + 1$ so-called magnetic levels; transitions then occur between those levels obeying the selection rule $\Delta M = 1, -1, 0$, with the restriction that if $\Delta J = 0$ the combination $M = 0$ to $M = 0$ is forbidden. This can be shown most conveniently by a diagram. Taking, for example, $J_1 = 3$ and $J_2 = 2$ we write the following two rows, the upper one the possible values of the product M_1g_1 and the lower the products M_2g_2:

$$\begin{tikzcd}
M_1g_1(J_1 = 3) & 3g_1 \arrow[dr] & 2g_1 \arrow[d] \arrow[dr] & 1g_1 \arrow[dl] \arrow[d] \arrow[dr] & 0 \arrow[dl] \arrow[d] \arrow[dr] & -1g_1 \arrow[dl] \arrow[d] \arrow[dr] & -2g_1 \arrow[dl] \arrow[d] & -3g_1 \arrow[dl] \\
M_2g_2(J_2 = 2) & & 2g_2 & 1g_2 & 0 & -1g_2 & -2g_2 &
\end{tikzcd}$$

The vertical arrows, for which $\Delta M = 0$, indicate the so-called π or parallel components of the Zeeman effect, for if the emitted light is examined at right angles to the field these components are found to be polarized with their electric vectors parallel to the magnetic field. The diagonal arrows, corresponding to $\Delta M = 1$ or -1, indicate the σ (*senkrecht* or perpendicular) components, which are polarized with their electric vectors perpendicular to the field. The deviation in units of oh, for a field of 1 gauss, of the emitted light from the original frequency is written symbolically

$$\pm(2g_1 - 2g_2, 1g_1 - 1g_2, 0), 3g_1 - 2g_2, 2g_1 - 1g_2, 1g_1, 1g_2, 2g_2 - 1g_1$$

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[1] Landé, *Zeits. Physik*, **15**, 189 (1923).

[2] Back and Landé, "Zeemaneffekt und Multiplettstruktur der Spektrallinien," pp. 42 and 198, Springer (1925).

[3] Ruark and Urey, "Atoms, Molecules, and Quanta," p. 319, McGraw-Hill (1930).

[4] Pauling and Goudsmit, "The Structure of Line Spectra," pp. 71 and 115, McGraw-Hill (1930).

[5] Hund, "Linienspektren und Periodisches System der Elemente," p. 106, Springer (1927).

where each difference corresponds to a single Zeeman component, the expressions in brackets indicating the π components and the others the σ components. The ± sign shows that the pattern is symmetrical about the original line. The original frequency appears in the π group; it is completely lacking for those lines due to combinations between terms of even multiplicity (for then J has half-integral values, and so M cannot be zero), and also for terms of odd multiplicity if $\Delta J = 0$, because in this special case the transition $M = 0$ to $M = 0$ is forbidden. The order of magnitude of the Zeeman pattern separation is a few Lorentz units per gauss, amounting to one or two wave numbers for a field of, say, 20,000 gauss.

It is of interest to observe how the above method of calculating Zeeman patterns always gives the original line plus two symmetrically placed companions for combinations between singlet terms. For these terms $S = 0$, hence $g = 1$. For the combination ${}^1F_3 - {}^1D_2$, to which the above diagram would apply, we obtain $\pm(0, 0, 0)\ 1, 1, 1, 1, 1$, *i.e.*, $\pm(0)\ 1$, the original line in the π polarization, and the two satellites in the σ polarization one Lorentz unit away per unit field. We also observe that g may equal zero, as in the cases ${}^5F_1$, ${}^7H_2$, ${}^4D_{\frac{1}{2}}$, ${}^6G_{\frac{3}{2}}$, ${}^8I_{\frac{5}{2}}$, etc., or it may be indeterminate as for ${}^1S_0$, ${}^3P_0$, ${}^5D_0$, ${}^7F_0$, etc. Lines involving terms whose g values are 0 and 0, or 0 and 0/0, (indeterminate), show no Zeeman splitting as the above theory indicates. Extensive tables giving the theoretical Zeeman patterns, for L-S coupling, that are likely to occur in the spectra of elements other than the rare earths, have been published by Kiess and Meggers.[1] A detailed discussion of the whole subject of the Zeeman effect including the theoretical and experimental work, j-j coupling, and strong coupling with the magnetic field (Paschen-Back effect) is given by Back and Landé,[2] and by Pauling and Goudsmit.[3]

7-8. The Stern-Gerlach Effect and Gyromagnetic Anomaly.

—Additional and independent evidence that atoms possess magnetic moments is given by the Stern-Gerlach effect. The experimental results are in excellent agreement with the theoretical predictions which are based on the same assumptions as those made in accounting for the anomalous Zeeman effect. The experiment consists in observing the lateral displacement of a beam of neutral atoms which passes through an inhomogeneous magnetic field. If an atom with a magnetic moment μ is placed in a uniform magnetic field H, it experiences merely a couple; if the field is not uniform, however, one pole of the elementary magnet, which may be taken as representing the atom, is acted on by a greater force than is the other and a translational motion of the magnet as a whole results.

The displacement to be expected for an atomic beam passing through a non-uniform magnetic field may readily be calculated. The energy of a magnet of moment, μ, in a field of strength, H, is

$$E = -\mu H \cos(\mu H)$$

where (μH) is the angle between the field and the axis of the magnet. The force on the magnet, say in the x direction, is thus

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[1] Kiess and Meggers, *Bur. Standards J. Res.*, **1,** 641 (1928).

[2] Back and Landé, "Zeemaneffekt und Multiplettstruktur der Spektrallinien," Springer (1925).

[3] Pauling and Goudsmit, "The Structure of Line Spectra," McGraw-Hill (1930).

$$F_x = -\frac{dE}{dx} = \frac{d(\mu H \cos(\mu H))}{dx}$$

If the component of the magnetic moment along H is constant, which is the case if μ is associated with an angular momentum, and if μ itself is a constant, the expression becomes

$$F_x = \mu \cos(\mu H)\frac{dH}{dx}$$

which shows that the force is zero unless the strength of the field varies with x, *i.e.*, unless the field is inhomogeneous along x. If such is the case the acceleration of the magnet along x is

$$a_x = \frac{F_x}{M} = \frac{\mu \cos(\mu H)}{M}\frac{dH}{dx}$$

where M is the mass of the magnet. If the atom magnet starts from the origin of coordinates with no x component of velocity, the displacement at the end of a time t is

$$d_x = \frac{1}{2}a_x t^2 = \frac{\mu \cos(\mu H)}{2M}\frac{dH}{dx}t^2$$

If the atoms in the beam are moving with a velocity v_z along the z-axis perpendicular to the inhomogeneity of the field and if the length of path in the field is l_z, then t, which is the time of flight, is equal to l_z/v_z, and the displacement along the x-axis on leaving the field is:

$$d_x = \frac{\mu \cos(\mu H)}{2M}\frac{dH}{dx}\frac{l_z^2}{v_z^2}$$

A beam of atoms, which are suspected of having a magnetic moment, is allowed to pass in the z direction through an inhomogeneous magnetic field and is caught on a suitably prepared recording plate. The mass M is known; the distance l_z and the displacement d_x, if any, may be measured directly; dH/dx may be determined by a fluxmeter or its equivalent, and v_z may be computed from kinetic theory in terms of the measured temperature of the source of the atoms. The quantity $\mu \cos(\mu H)$ may thus be calculated.

The classical theory of electrodynamics lays no restriction on the possible values of the angle (μH); all values between 0° and 180° are possible, so that the displacement d_x should cover a continuous range. The quantum theory postulates that the angular momentum of an atom, and consequently its magnetic moment, must be quantized, not only in magnitude but also in orientation with respect to the magnetic field. Indirect evidence for space quantization has been supplied by the success of the vector atom model in dealing with the Zeeman effect, but the above considerations offer a direct crucial test. If the quantum theory is correct, instead of obtaining a continuous range of displacements, only those corresponding to the allowed values of the quantity $\mu \cos (\mu H)$ will be observed. The experiment was first carried out by Stern and Gerlach[1] in 1924 using silver atoms. The results showed definitely that the atomic beam was split into two components, one on either side of the original direction. The quantity $\mu \cos (\mu H)$ was shown to have the value of plus or minus one Bohr magneton, indicating that the normal silver atom possesses a magnetic moment of one Bohr magneton and that its orientation with respect to the field can be only parallel or antiparallel. This is in complete accord with the experimental and theoretical spectroscopic results which agree in assigning the normal level of silver to the type ${}^2S_{\frac{1}{2}}$, which has the g value of 2. The magnetic field breaks up each atomic level into $2J + 1$ components separated from one another in energy by

$$goh = g\frac{eH}{4\pi m_0}h = g\frac{eh}{4\pi m_0}H$$

i.e., by g Bohr magneton gausses. The $2J + 1$ components arise from the space quantization of the angular momentum vector J, its projections along H being given by the quantum numbers M. Hence the only possible values of $\mu \cos (\mu H)$, the projections of the magnetic moment along the field, are

$$\mu \cos (\mu H) = Mg$$

For the ${}^2S_{\frac{1}{2}}$ state of silver, with $g = 2$, we have

$$\mu \cos (\mu H) = \tfrac{1}{2} \times 2 \text{ or } -\tfrac{1}{2} \times 2 = 1 \text{ or } -1$$

which as we have seen agrees with the experimentally observed value of this quantity for silver.

Similar experiments have been carried out using quite a number of different elements; the results confirm the Mg values for the normal states, found or predicted spectroscopically, with an accuracy of about 4 per cent. If the J value of the normal state is previously known, it is always possible to determine g experimentally by this method. The lack of complete uniformity of the velocities of the atoms in the beam causes a certain diffuseness in the observed patterns; this renders the interpretation difficult if the value of J is not known. For some elements, such as bismuth, the pattern indicates that g should be calculated on the assumption of j-j coupling rather than on the L-S type. It is of interest to note that these experiments give directly the g value of one level, whereas the Zeeman effect gives a pattern that depends on the g values of two levels. A very complete and interesting account of this work has been given by Fraser.[2]

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[1] Stern and Gerlach, *Ann. Physik*, **74**, 673 (1924).

[2] Fraser, "Molecular Rays," Cambridge University Press (1931).

A further point of interest in connection with the quantity g is its bearing on the so-called gyromagnetic anomaly. This is a phenomenon connected with the mechanical and magnetic moments of matter in bulk. If by magnetization a magnetic moment μ is given to a sample of matter, and if the ratio of this magnetic moment to the associated mechanical moment is g, an angular momentum equal to μ/g should appear on magnetization. On the straightforward classical theory it may be shown, as in the case of the orbital motion of an electron, that the value of g should be 1. The experiments of Barnett,[1] Chattock and Bates,[2] and others, on those ferromagnetic elements such as iron, cobalt, and nickel, which are capable of acquiring large magnetic moments, have shown that this ratio is not 1 but 2 to within the limits of experimental error. This means that for these substances, at least, the quantity g is equal to 2. This is the value of g associated with an S state or with a free electron whose only magnetic moment is that associated with its spin. The theory of ferromagnetism as developed by Heisenberg[3] attributes the phenomenon to the action of free electrons in the crystal lattice. As 2 is the g value for a free electron, the experiments which have been mentioned support this theory. Experiments have also been performed by Sucksmith[4] on paramagnetic substances for which different values of g would be expected since the orbital motion of the electrons contributes to the magnetic moment. The results are in good agreement with the theoretical predictions.

7-9. Wave-length Measurement with a Grating.—In principle the absolute value of the wave length of light may be determined by means of a diffraction grating. To review briefly the theory of this instrument, let us recall that if plane parallel light of wave length λ is incident at an angle θ_i on a plane made of alternate strips of opaque and transparent material, such as a grating ruled on glass, where the furrows ploughed by a diamond point are the opaque regions, the open spaces act as elementary sources of spherical waves which advance in all directions in accordance with Huygens' principle. Constructive interference takes place in those directions in which the waves from the different openings are in phase, *i.e.*, in those directions for which the path difference between adjacent openings is a whole number of wave lengths. If D is the grating constant (the distance between corresponding points of neighboring openings), the condition for constructive interference is expressed by the equation

$$n\lambda = D\,(\sin\theta_r \pm \sin\theta_i) \tag{7-22}$$

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[1] BARNETT S. J. and L. J. H., *Phys. Rev.*, **17**, 404 (1921); **20**, 90 (1922); *Physik. Zeits.*, **24**, 14 (1923).

[2] CHATTOCK and BATES, *Phil. Trans.*, **223**, 257 (1922).

[3] HEISENBERG, *Zeits. Physik*, **49**, 619 (1928).

[4] SUCKSMITH, *Proc. Roy. Soc.*, **128**, 276 (1930); **133**, 179 (1931).

where the integer n is called the order of the spectrum while θ_r and θ_i are the angles that the diffracted and incident beams make with the normal to the grating surface. The positive or negative sign is used depending on whether the incident and refracted beams lie on the same or different sides of the normal to the grating. A similar equation holds for a reflection grating. All these quantities except λ are directly measurable, in theory, so that λ may be determined. In practice absolute measurements are not easy to make, for the determination of the grating constant to the required degree of accuracy is difficult, even supposing for the moment that it really is a constant. However, making this assumption, it is evident that relative wave lengths can be determined to the accuracy with which the angles can be measured; the absolute values can be found subsequently by an exact determination of the grating space or by some independent absolute measurement of one wave length.

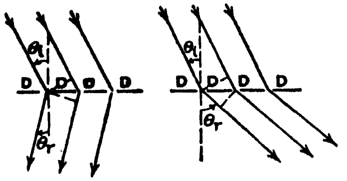

FIG. 7-6.—The principle of the diffraction grating.

In photographic spectroscopy the angles are not measured directly, but rather the distances along the plate from one image to another; wave lengths may then be interpolated between lines of known wave length. It is obvious from Eq. (7-22) that a line of say 9000 Å should fall on the plate in the first order at exactly the same place that a line of 4500 Å will appear in the second order. Or putting it another way, if the wave length of a line is known very precisely to be 9000 Å, this is equivalent to knowing, with even greater precision, lines at 4500 Å, 3000 Å, 2250 Å, etc. Thus by the superposition of orders a single well-determined wave length may be used as a reference point in regions of shorter or longer wave length. This was the procedure adopted by Rowland in the eighteen-eighties when he measured the wave lengths of the absorption lines in the solar spectrum with a grating. One of the sodium yellow lines (D_1) was used as the primary standard, with 5896.156×10^{-8} cm. taken as the best average value of the wave length as previously determined by several observers who had directly measured their grating constants. As will be presently explained, Rowland's apparatus was such that, for relatively small wave-length ranges, the distance along the photographic plate was directly proportional to the wave-length change, so that interpolation between lines could be made very accurately. It was thus anticipated, in view of the principle of superposition and the fact that the spectrum was a so-called normal one, that any future redeterminations of the sodium line would merely involve correcting all of Rowland's wave lengths by one multiplicative factor.

This hope was blasted by the work of Michelson and Benoit,[1] and of Fabry and Perot,[2] who, about 1895, measured the wave length of the cadmium red line with an interferometer. In principle, though not in detail, the method consists in counting the number of wave lengths of this color that lie within 1 meter by observing the number of interference fringes that cross a fiducial mark when one plate of an interferometer is drawn away from the other through a measured distance. The primary standard was thus determined and it is taken to be

Cadmium red line = 6438.4696 International Ångström units

in dry air at a pressure of 760 mm. Hg, 15° C., and with the gravitational constant equal to 980.67 cm. sec.$^{-2}$. By choosing to call this an exact value, the International Ångström (IÅ) is thus defined. The previous Ångström unit had been defined as 10^{-8} cm., so that no spectral line could be expected to be given exactly by a finite number of figures in that unit. For most work this fine distinction is unimportant, for the International Ångström equals 10^{-8} cm. to within 1 part in 10^7. Further interferometer measurements on lines from an iron arc were made, using the cadmium red line as the primary standard, thus supplying secondary standards. Tertiary standards have been established by careful interpolation between the secondary standards from good grating spectrograms. The result of these interferometer measurements was to show that one factor was not sufficient to correct the Rowland wave lengths; the correction varied in magnitude throughout the spectrum. Tables of the corrections to reduce Rowland's values, which appear in all the older literature, to International Ångström units have been given by Baly[3] and Fowler.[4] An error may possibly have been introduced through Rowland's ignorance of the wave-length differences in solar and terrestrial lines, due to various causes. Furthermore, Kayser[5] experimentally demonstrated by careful measurements with two Rowland concave gratings that the principle of superposition did not hold to the high degree of accuracy desired. The discrepancy apparently lay in irregularities in the grating spacing. Parenthetically, it may be remarked that no gratings as good as Rowland's best have ever been made since.

All modern spectroscopic work is performed on the basis of these international primary, secondary, and tertiary standards by various methods of interpolation, both with gratings and with prisms. The combination of interferometric and spectroscopic methods in the hands of experienced workers has extended the list of accurate reference points well down toward 2000 IÅ. Other standards may be inferred by the use of the combination principle; accurate term values are calculated from lines which lie within the range of measured standards, and hence the wave lengths of lines due to different combinations of these same terms may be computed with equal exactness in spectral regions remote from the standards. In comparing an unknown spectrum with a standard one both are photographed on the same plate, recognition of the two spectra being facilitated by using shutters of different lengths over the slit.

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[1] Michelson and Benoit, *Mém. Bur. Int. Poids et Mès.*, **2**, 1 (1895).

[2] Fabry and Perot, *Ann. Chim. et de Physique*, **16**, 289 (1899).

[3] Baly, "Spectroscopy," Longmans (1929).

[4] Fowler, "Report on Series and Line Spectra," Fleetway Press (1922).

[5] Kayser, *Astrophys. J.*, **19**, 157 (1904).

The plane grating, whether of the transmission or reflection type, requires the use of a lens to collimate the light from the slit and a second lens to focus the diffracted rays on the photographic plate or eyepiece. This is a great disadvantage since it limits the use of gratings with glass lenses to wave lengths above about 3500 Å, for most glasses are highly absorbing for shorter wave lengths. Quartz lenses extend the range to about 1800 Å, and fluorite lenses several hundred Ångströms further, but large lenses of these materials are very rare and expensive. Rowland's introduction of the concave grating, in 1881, was a highly important advance. A concave mirror of glass or metal may be used to form an image of the slit directly on the photographic plate; if this mirror is ruled after the manner of a plane grating, the single "white" image of the slit is dispersed into a spectrum of its component colors. The rulings are not great circles but rather the projection of a plane grating on the spherical surface. This arrangement has one disadvantage for certain kinds of work and this is that it is not stigmatic; light from each point of the slit reaches a range of points on each image. This, however, is important only when it is desired to distinguish between the different regions of the illuminated slit, which is not generally the case.

As is shown in treatises on optics, if the slit and the grating are located on the circumference of a circle whose diameter is equal to the radius of curvature of the grating, all the lines of all orders are brought to a focus on this circle. It is this constancy of focus for all orders that permits their superposition; with a plane grating and lens this is not the case because complete achromatization cannot be obtained. In the Paschen type of mounting, the slit and grating are fixed in position and photographic plates are placed along the focal circle. Only those rays which leave the grating almost normally fall normally on a plate. For these rays the angle of diffraction, θ_r, is almost zero, so that Eq. (7-22) becomes to a good approximation,

$$n\lambda = D(\theta_r \pm \sin \theta_i)$$

But $\theta_r = LR$, where L is the distance along the plate from the intersection with the grating normal, and R is the distance from the plate to the grating. Hence

$$\begin{aligned}\lambda &= \frac{D}{n}\sin\theta_i + \frac{DR}{n}L \\ &= \text{constant} + \text{constant} \times L\end{aligned}$$

Therefore the wave length is directly proportional to the distance along the photographic plate for those rays which lie almost along the normal to the grating. Interpolation between standard wave lengths is then very simple for this "normal" portion of the spectrum. For other regions of the spectrum the relationship is not linear, nor does the light fall perpendicularly on the plates. Any unevenness of the glass causes local compression or stretching of the dispersion. It is therefore necessary to plot a curve of position on the plate against the wave length for the known standards, or, better still, a curve may be drawn representing the difference between a strictly linear relation and the known standard wave lengths.

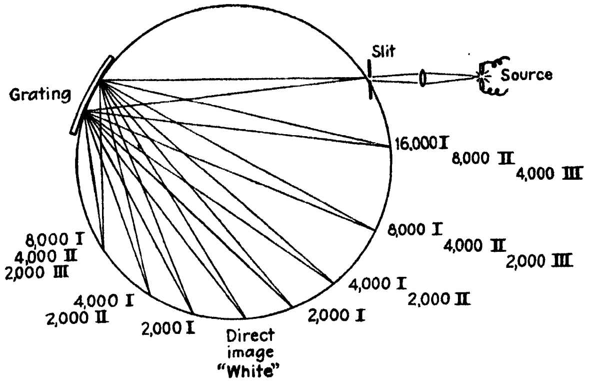

FIG. 7-7.—A diagrammatic sketch of the Paschen mounting for a concave diffraction grating. The principle of superposition of orders, given by roman numerals, is indicated. With this particular arrangement, a "normal" spectrum is obtained only in the region around 8,000 I, 4,000 II, 2,000 III on the right. Not to scale.

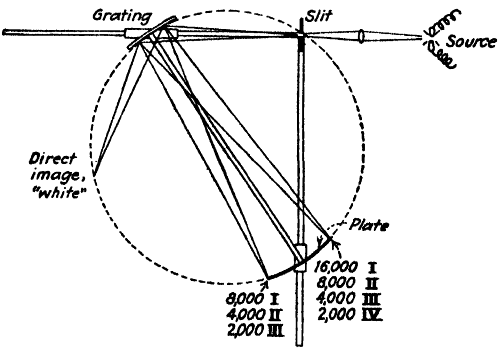

FIG. 7-8.—A sketch of the Rowland mounting for a concave grating. The region being photographed always forms a "normal" spectrum. Not to scale.

By giving up the somewhat doubtful advantage of being able to photograph simultaneously the entire spectrum in many orders, as is the case with the Paschen mounting, Rowland was able to devise an arrangement whereby the particular region being photographed is always normal to the grating and hence the wave length always proportional to the distance along the plate. In the Rowland mounting the slit is located at the junction of two mutually perpendicular tracks. On each of these is a truck and these trucks carry on bearings the two ends of a beam of length equal to the diameter of the Paschen circle, *i.e.*, the radius of curvature of the concave grating. The grating and plate are placed perpendicularly to the length of this beam at its two ends. The slit, grating, and plate thus always remain on the circumference of the Paschen circle. The device is obviously equivalent to having a movable slit capable of traveling around the Paschen mounting.

7-10. Wave-length Measurement with a Prism.—Due to the nature of the variation of the index of refraction with wave length, the spectrum produced by a prism does not give a linear variation of either wave length or wave number with position along the photographic plate. Direct linear interpolation between standards is therefore impossible except over extremely small ranges. We shall briefly review several indirect but accurate interpolation methods which have been developed. They all involve a considerable amount of multiplication or division so that a computing machine is almost a necessity. If one is not available rough results, to 10 or 20 Å, may be obtained by plotting the wave lengths of as many standards as possible against position on the photographic plate and drawing a smooth curve through them. Wave numbers may be plotted instead of wave lengths and in this case the curve is more nearly linear, which facilitates interpolation. It is desirable to plot such a curve in any case, for it helps to avoid gross errors in identifying lines to be used as standards.

In the early days of the prism spectroscope, use was made of the Cauchy dispersion formula

$$n = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4}$$

where n is the refractive index of the prism, and a, b, and c are constants to be determined from known wave lengths. At minimum deviation, the index is connected with the angle of the prism A and the angle of deviation ϕ by the relation [see Eq. (2-41)]

$$n = \frac{\sin\left(\dfrac{A + \phi}{2}\right)}{\sin\dfrac{A}{2}}$$

Hence by measuring A and ϕ the wave length can be computed over a range within which the different colors may all be taken as having passed through the prism at minimum deviation.

Hartmann Method.—The very laborious process indicated above was eliminated by Hartmann,[1] in 1898, who showed that the expression

$$n = C' + \frac{B'}{(\lambda - A')^p}$$

represents with sufficient accuracy the dependence of n on λ over a rather wide range. The quantities A', B', and C' are constants, while p has the value 1.2 for prisms made of crown or flint glass. Solving this equation for λ we obtain

$$\lambda = A' + \frac{B'^{\frac{1}{p}}}{(n - C')^{\frac{1}{p}}}$$

A further simplification is possible if p is set equal to unity and the index of refraction is replaced by the linear distance L of a spectral line along the plate, measured from any arbitrary zero. We then have

$$\lambda = A + \frac{B}{L - C}$$

This expression holds with remarkable accuracy; over a range of 1000 Å the average error may be as small as 0.1 Å. The constants A, B, and C are found by solving simultaneously the three equations for three standard lines, located preferably at the two ends and the middle of the range. The solution is conveniently performed in the following manner:

$$\lambda_1 = A + \frac{B}{L_1 - C} \tag{7-23}$$

$$\lambda_2 = A + \frac{B}{L_2 - C} \tag{7-24}$$

$$\lambda_3 = A + \frac{B}{L_3 - C} \tag{7-25}$$

Subtracting Eq. (7-23) from Eqs. (7-24) and (7-25) and rearranging, we obtain

$$C^2 - (L_1 + L_2)C + L_1L_2 = \frac{L_1 - L_2}{\lambda_2 - \lambda_1}B \tag{7-26}$$

$$C^2 - (L_1 + L_3)C + L_1L_3 = \frac{L_1 - L_3}{\lambda_3 - \lambda_1}B \tag{7-27}$$

Subtracting Eq. (7-27) from Eq. (7-26) and solving for B, we have

$$B = \frac{(L_2 - L_3)(L_1 - C)}{K} \tag{7-28}$$

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[1] HARTMANN, *Astrophys. J.*, **8**, 218 (1898).

where

$$K = \frac{(L_1 - L_2)}{\lambda_2 - \lambda_1} - \frac{(L_1 - L_3)}{\lambda_3 - \lambda_1} \tag{7-29}$$

Eliminating B between Eqs. (7-23) and (7-28) and solving for A,

$$A = \lambda_1 - \frac{(L_2 - L_3)}{K} \tag{7-30}$$

Eliminating A and B between Eqs. (7-24), (7-28), and (7-29) and solving for C,

$$C = L_2 + \frac{(L_2 - L_3)}{K}\frac{(L_1 - L_2)}{\lambda_1 - \lambda_2} \tag{7-31}$$

Equations (7-28) to (7-31), are perfectly general and may be used at once to determine the numerical values of A, B, and C in terms of the known wave lengths λ_1, λ_2, and λ_3 and their corresponding traveling microscope readings L_1, L_2, and L_3. (Note that the quantity $(L_2 - L_3)/K$ occurs three times and hence its separate evaluation is of advantage.) Care should be taken with the signs of the quantities evaluated; it is wise to check the final equation by calculating the three standard wave lengths before proceeding to the unknown lines.

The Hartmann formula is highly satisfactory and requires but three standard lines, yet it is a little cumbersome to use, since a new divisor must be found for each line, and the dividend B of six or seven significant figures must be set up anew on the calculating machine each time.

Russell-Shenstone Method.—A quick method of reducing prismatic spectra, which is superior to the Hartmann method when a spectrum containing a large number of lines is to be measured, has been developed by Russell and Shenstone.[1] The process is purely empirical and will not work on certain instruments, but a few minutes spent in testing it is well worth the time. It has the disadvantage of requiring a large number of standard lines, but the advantages of rapidity and the ability to take care of fluctuations in the surface of the photographic plate. Furthermore it deals directly in wave numbers, which are the ultimate desiderata.

Essentially the method is one of successive approximations. A linear interpolation of the wave numbers of the standard lines is made:

$$\tilde{\nu}_{\text{lin.}} = \frac{\tilde{\nu}_2 - \tilde{\nu}_1}{L_2 - L_1} \times \Delta L + \tilde{\nu}_1 \tag{7-32}$$

where $\tilde{\nu}_1$ and $\tilde{\nu}_2$ are the wave numbers of the standards at the two ends of the range, L_1 and L_2 are their corresponding traveling-microscope readings, and ΔL is the difference between the scale reading for an intermediate standard line and L_1. (The scale reading L should increase with the wave number.) It is observed that $\tilde{\nu}_{\text{lin.}}$ is less than the true value $\tilde{\nu}$ except at the ends of the range, and a curve is plotted of $\tilde{\nu} - \tilde{\nu}_{\text{lin.}}$

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[1] RUSSELL and SHENSTONE, *J. Optical Soc. Am.*, **16**, 298 (1928).

against the scale reading L. The range covered should not be so large that the maximum value M of this curve is greater than about 100 wave numbers.

This first correction $\tilde{\nu} - \tilde{\nu}_{\text{lin.}}$ is then assumed to vary parabolically with L, and its value is calculated for each line in the following manner: Taking the origin of coordinates at the point O, whose abscissa and ordinate on the old scale are $(L_2 - L_1)/2$ and M, respectively, the equation for the parabolic approximation may be written

$$y = Ax^2 \tag{7-33}$$

A is determined from the two end points by the relation

$$A = \frac{y}{x^2} = \frac{M}{\left(\dfrac{L_2 - L_1}{2}\right)^2}$$

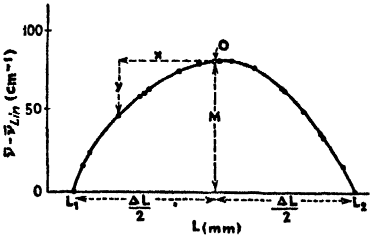

FIG. 7-9.—A typical first correction curve for standard lines in the Russell-Shenstone method of reducing prismatic spectra. The difference between the true wave number and that calculated linearly is plotted against the position on the plate.

The value of x for each standard is next found by subtracting its L from the mid-point of the scale range; the appropriate y for each standard is then found from Eq. (7-33). This may be performed in one operation on a 20-in. slide rule to sufficient accuracy. The wave number calculated on the parabolic assumption $\tilde{\nu}_{\text{par.}}$, for each standard is determined from the equation

$$\tilde{\nu}_{\text{par.}} = \tilde{\nu}_{\text{lin.}} + M - y \tag{7-34}$$

It will be found that $\tilde{\nu}_{\text{par.}}$ does not agree exactly with the known wave numbers, but the maximum departure should not be greater than about one wave number. A second correction curve is then drawn, plotting $\tilde{\nu} - \tilde{\nu}_{\text{par.}}$ against the scale reading L for all the standards. This curve is due to higher order terms, since $\tilde{\nu} - \tilde{\nu}_{\text{lin.}}$ is not strictly parabolic. The form of the curve is quite sensitive to the chosen location of the origin O. Sometimes the curve shows marked asymmetries, which indicate local depressions or humps in the photographic plate. In prism instruments with simple lenses, the light falls on the plate at a considerable angle with the normal, so that a slight surface irregularity causes a considerable shift in the position of the image. Since both the standards and the unknown lines in the same vicinity are affected by these variations, there is no error due to this cause in the Russell-Shenstone method, while the Hartmann formula is only correct for a perfectly smooth plate.

Having found that the standard lines give a consistent second-order correction curve, the calculation of the unknown lines may be accomplished rapidly. All that is required is the calculation first of $\tilde{\nu}_{\text{lin.}}$ then of $\tilde{\nu}_{\text{par.}}$ and the addition of a small correction read graphically from the second curve. The work is greatly simplified with a calculating machine capable of performing the operation

$$u = \alpha + \beta v$$

where α and β are constants and u and v are variables. The quantity α has the value $M + \tilde{\nu}_1$, while β is the linear dispersion constant $(\tilde{\nu}_2 - \tilde{\nu}_1)/(L_2 - L_1)$ which is set up once and for all as the multiplicand on the machine. With the multiplier keys set at the value L_1, the resultant is set to equal $\tilde{\nu}_1 + M$, so that as the multiplier is set successively at different values of L the quantity

$$\tilde{\nu}_1 + M + \frac{\tilde{\nu}_2 - \tilde{\nu}_1}{L_2 - L_1} \times L$$

is determined. Subtracting the appropriate value of y from this gives $\tilde{\nu}_{\text{par.}}$, and on adding the small correction read from the second curve, the final wave number is obtained. This avoids the necessity of finding ΔL for each line. Aside from the original scale readings, all that is required is a table of the values of x, the distance of the line along the plate from the mid-point of the range.

General Technique.—In measuring a plate with a traveling microscope it is essential always to approach a line from the same side, in order to avoid back-lash in the screw. If the line is overrun the screw should be backed off several turns and another approach made. To guard against the very common personal error of consistently setting a little beyond or short of a line, as well as to average out the irregularities of the screw, it is worth while to measure each plate twice, in opposite directions, by turning the plate around and advancing the microscope in the same direction as before. The two resulting sets of readings then increase in value toward opposite ends of the spectrum; they may be reduced to a single average by subtracting one set from the other (which is increased by some constant such as 100, so that the difference is always positive). This gives a dispersion constant of half as many wave numbers per millimeter as is actually the case, but this is immaterial if all calculations are made consistently on this basis.

It must be recalled that, except in vacuum spectroscopes, the wave length measured is that in air, and as the velocity of light in air depends upon the wave length, a variable correction must be applied in order to get the vacuum wave length or wave number. Since the wave length for a given frequency is proportional to the velocity of propagation, and since n, the index of refraction, is the ratio of the velocity in a vacuum to the velocity in the medium, we have

$$\lambda_{\text{vac.}} = n\lambda_{\text{air}}$$

Therefore

$$\lambda_{\text{vac.}} - \lambda_{\text{air}} = n\lambda_{\text{air}} - \lambda_{\text{air}} = (n - 1)\lambda_{\text{air}}$$

Hence to find $\lambda_{\text{vac.}}$ we add to λ_{air} the product $(n - 1)\lambda_{\text{air}}$. The values of n for air have been accurately measured by Meggers and Peters.[1] A very convenient set of tables has been published by Kayser[2] in which λ_{air} is directly changed to wave numbers in vacuum ($\tilde{\nu}_{\text{vac.}} = 1/\lambda_{\text{vac.}}$) through the above mentioned values of the index of refraction for the range from 10,000 Å to 2000 Å. The magnitude of the error involved in merely taking $1/\lambda_{\text{air}}$ as the wave number is 1.5 Å or 4.2 wave numbers at 6000 Å, and 0.9 Å or 10 wave numbers at 3000 Å. Hence the correction to vacuum is trivial for measurements made on a small prism instrument.

7-11. Experiment on Wave-length Measurement.—With the proper technique the most accurate absolute value of a wave length can be obtained with an interferometer. In the Michelson form, a single wave length, such as the cadmium red line, enters the instrument, and the fringes passing a fiducial mark are counted as one plate is moved perpendicularly to its surface through a known distance. A shift of one fringe corresponds to a motion of this plate of half a wave length. The details for the absolute determination of a wave length by this method are given by Fabry and Perot.[3] In practice with an ordinary interferometer it is very difficult to obtain really accurate values of wave length by any simple procedure. As an example, the mercury green line, $\lambda = 5460$, may be isolated by the Wratten filter 77-*A* and its fringes counted as one plate of the interferometer is moved relatively to the other. The change in path may be measured by observing a stage-micrometer scale, which is clamped to the moving system, through a microscope equipped with cross hairs. But as the accuracy of setting is, say, 0.001 mm., which corresponds to a displacement of four fringes, 20,000 fringes must be counted to obtain a value of the wave length correct to 1 Å, *i.e.*, 1 part in 5000. An accuracy of 0.5 per cent can be obtained by counting 800 to 1000 fringes, which can be done in about half an hour without undue fatigue.

Since precise measurements with an interferometer are difficult and tedious, it is more satisfactory for our purposes to obtain absolute measurements with a grating where an accuracy of a few hundredths of a per cent can readily be achieved. The simplest arrangement to use is a plane transmission grating mounted on an ordinary spectrometer table with the light incident normally upon its surface. The equation for the grating then becomes:

$$n\lambda = D \sin \theta_r$$

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[1] Meggers and Peters, *Bur. Standards Bull.*, **14**, 697 (1917); *Astrophys. J.*, **50**, 56 (1919).

[2] Kayser, "Tabelle der Schwingungszahlen," Hirzel (1925).

[3] Fabry and Perot, *Ann. Chim. et de Physique*, **16**, 289 (1899).

The grating constant D is ideally determined by observing the diffraction angle for the same wave length as was used in the interferometer measurement and applying the grating equation. Since for practical reasons only moderate accuracy can be expected by this method, it is preferable to measure the grating constant directly by the use of a good microscope equipped with a micrometer eyepiece. The grating is placed, rulings uppermost, on the microscope stage and illuminated in the usual way. Care must be taken that the objective of the microscope does not come in contact with the surface of the grating when the focusing adjustments are being made, as this would injure the rulings, particularly of a replica grating. Several hundred lines should be measured in groups of ten to prevent a miscount. The eyepiece-micrometer screw may be calibrated by measuring a standard stage-micrometer scale.

The necessary adjustments of the telescope, grating, and collimator in setting up a plane transmission grating spectrometer may be briefly summarized as follows. The Gauss eyepiece of the telescope is first focused on the cross hairs, and then the cross hairs and eyepiece together are adjusted for parallel light by focusing the telescope on some distant object through an open window. No parallax, *i.e.*, relative motion of the images of the cross hairs and distant object, should be observed as the head is moved from side to side. The telescope is then replaced in the instrument and the collimator focused until a sharp image of the slit is seen when the telescope and collimator are in line. The grating is then mounted with the ruled side away from the collimator, directly over the axis of the turntable and parallel to the line joining two of the three leveling screws. The Gauss eyepiece is then illuminated and the tilt of the grating and telescope adjusted until the image of the cross hairs, seen by reflection from the grating, coincide with the cross hairs themselves. The grating is then rotated through 180° and this coincidence again brought about, making half the adjustment by tilting the grating and half by tilting the telescope. This procedure is repeated till the images stay in coincidence. The telescope is then perpendicular to the axis of the turntable and the grating parallel to it. The collimator is made parallel to the telescope by adjusting its tilt until the image of a fine wire stretched across the middle of the slit coincides with the intersection of the cross hairs. The angular position, θ_0, of the telescope circle is read when the image of the slit is on the cross hairs, and the telescope is then turned through 90°. The grating table is rotated till the directly reflected image of the slit is seen at the intersection of the cross hairs; turning the grating table back through 45° then puts the grating normal to the incident light. If there is no scale on the grating table, this adjustment can be made by illuminating the Gauss eyepiece again with the telescope in the θ_0 position and rotating the grating till coincidence between the cross hairs and their reflected image from the surface of the grating is obtained. The rulings are made parallel to the table axis by adjusting the leveling feet under the grating, until the image of the wire across the slit, as seen in the various diffracted orders to the right and left of the central image, remains at the level of the cross-hair intersection. After this adjustment the alignment of the grating on the axis of rotation should be rechecked. Finally, the slit, which should be made very narrow, is adjusted to be parallel to the grating rulings by observing one of the diffracted images and rotating the slit until the image appears sharpest.

A convenient source to use with the grating is a quartz or glass mercury arc; it has many strong lines widely dispersed throughout the visible spectrum and these arcs, which are readily obtained, are very constant and reliable. These sources may be placed directly in front of the slit, or an image of them may be cast on it by means of a condensing lens. The angular settings of the telescope are then measured as accurately as possible when the cross hairs are brought into coincidence with the diffracted images of the slit for 10 or 12 of the strongest mercury lines. As many orders as possible should be used on both sides of the central image. To reduce the percentage error in reading the scale, the diffraction angle θ_r, for any wave length, in a given order, should be taken as half the difference between the scale readings when set on the images in the right and left orders. As the accuracy of measurement increases with the order, the highest order in which the line can be accurately set upon should be used in the calculation of its wave length. Results accurate to within 2 Å or 3 Å can be obtained even with an inexpensive replica grating when used in the second order.

These mercury lines whose wave lengths have been measured with a grating can be used as standards for determining the wave lengths of the weaker mercury lines and also of lines in other spectra if a mercury comparison spectrum is photographed over the unknown spectrum. The photographs are most conveniently made with a prism instrument, for, as all the light contributes to the formation of a single spectrum, the intensity is greater than with a grating. Small instruments, such as the quartz Hilger E-31 or Gaertner L-250 for the ultra-violet or the constant-deviation Hilger D-77 or Gaertner L-230 for the visible, are satisfactory for the analysis of the following sections. The slit should be made as fine as possible and a series of focusing exposures taken varying the two adjustments, collimator focus and plate angle, separately. The plates are then examined for the best focus and the pertinent data recorded. Rapid panchromatic plates such as the Eastman Wratten and Wainwright plates, or the Ilford special rapid panchromatic plates, are suitable for general spectroscopic work throughout the visible and near ultra-violet. The positions of the lines in the spectrum photographs may be measured with a traveling microscope or comparator capable of an accuracy of at least 0.01 mm. Using suitably spaced mercury lines as standards, the Hartmann formula can be applied as described in the previous section and the unknown wave lengths calculated. These are then transformed into air or vacuum wave numbers, and the spectrum is ready for analysis.

7-12. Experiment on the Spectrum of Atomic Hydrogen.—The discharge tube should be designed to produce, if possible, only the spectrum of atomic hydrogen in order to avoid the confusing lines from the molecule. For this purpose, a discharge tube about 1.5 meters long and 1 cm. in diameter may be used, bent into a U-shape for convenience. Nickel electrodes spot-welded to tungsten rods are sealed into bulbs at each end. These electrodes should be rather large to avoid excessive sputtering. A cylindrical shape is convenient. Hydrogen at a pressure of 5 or 6 mm. Hg is admitted to the tube from an electrolysis apparatus and a discharge run for several minutes, while the tube is still connected to the vacuum system to out-gas the electrodes at least partially. No effort should be made to make the tube or gas particularly clean; impurities apparently promote the production of the atomic spectrum. The discharge, when run on a small 10,000-volt transformer, varies in character in different parts of the tube and changes with time and temperature, but there is usually a region which emits the atomic spectrum with very few molecular lines. The successful operation of the tube depends to a certain extent on the current density; the optimum value can only be found by trial. The regions which emit the atomic spectrum strongly are generally near the middle of the tube and exhibit a red or purplish color; these may be examined with a hand spectroscope to be sure that the conditions are satisfactory before the tube is sealed off. If argon is available, a discharge may be run in the tube with this gas for a few minutes; it is then pumped out and hydrogen admitted as before. The argon poisons the glass in such a way that recombination of the hydrogen atoms on the walls of the tube is greatly reduced.[1] Further details of methods for obtaining the higher members of the Balmer series are given in the literature.[2]

An ordinary pyrex tube is sufficiently thin so that very little absorption of the ultra-violet members of the Balmer series occurs. If no quartz lens is available, the tube may be put directly in front of the slit of the spectroscope, though the use of a lens to form an image of the tube on the slit is to be recommended. Ten or eleven members of the Balmer series may be photographed quite easily with a small quartz prism spectroscope. An ordinary glass instrument is not satisfactory for this purpose as the lenses and prism absorb a great deal of the light of the higher series members, which are quite feeble to begin with. Quartz has the disadvantage, however, of having very small dispersion in the red so that the long-wavelength region is crowded together, thus reducing the accuracy of measurement. Exposures of from $\frac{1}{2}$ to 2 min. are generally quite adequate. The slit length is then reduced a trifle in order to identify the spectra, and a mercury arc is photographed for 2 or 3 sec. These lines are used as standards for calculating the wave numbers of the Balmer series.

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[1] LAU and REICHENHEIM, *Zeits. Physik*, **73**, 31 (1931).

[2] WOOD, *Proc. Roy. Soc.*, **97**, 455 (1920); *Phil. Mag.*, **42**, 729 (1921).
WHIDDINGTON, *Phil. Mag.*, **46**, 605 (1923).
HERZBERG, *Ann. Physik*, **84**, 553 (1927).
TAKAMINE and SUGA, *Sci. Papers Inst. Phys. and Chem. Res., Tokyo*, **24**, 117 (1930).

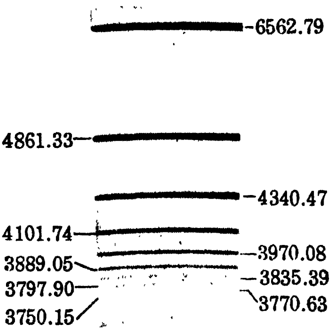

FIG. 7-10.—The Balmer series of atomic hydrogen, photographed with a small quartz spectrograph. Wave lengths are shown in Ångström units.

The Balmer series may be represented by the equation

$$\tilde{\nu} = \frac{R_{\mathrm{H}}}{4} - \frac{R_{\mathrm{H}}}{n^2}$$

where $n = 3, 4, 5, 6$, etc. Hence a plot of $\tilde{\nu}$ against $1/n^2$ should give a series of points through which a straight line may be drawn; the slope of this line is R_{H} and the intercept $R_{\mathrm{H}}/4$. This experimental value of R_{H} may be compared with the theoretical value

$$R_{\mathrm{H}} = \frac{2\pi^2 \mu e^4}{h^3 c}$$

where $\mu = mM/(m + M)$, m and M being the masses of the electron and proton, respectively, using the values of the constants that have been determined previously.

It is interesting to examine the completely calculable case of hydrogen from the viewpoint of the vector model. The single electron may be an s type so that there is the possible series of levels $1s\ ^2S_{\frac{1}{2}}$, $2s\ ^2S_{\frac{1}{2}}$, $3s\ ^2S_{\frac{1}{2}}$, etc., or it may be a p or d type giving the series $2p\ ^2P_{\frac{1}{2}}\ ^2P_{\frac{3}{2}}$, $3p\ ^2P_{\frac{1}{2}}\ ^2P_{\frac{3}{2}}$, etc., and $3d\ ^2D_{\frac{3}{2}}\ ^2D_{\frac{5}{2}}$, $4d\ ^2D_{\frac{3}{2}}\ ^2D_{\frac{5}{2}}$, etc., respectively. But for the two-body problem, the analysis shows that the energy of a level depends to a first approximation only on the total quantum number of the electron; hence the lowest state is $1s\ ^2S_{\frac{1}{2}}$; the next higher is $2s\ ^2S_{\frac{1}{2}}$, $2p\ ^2P_{\frac{1}{2}}\ ^2P_{\frac{3}{2}}$ (all three coincident); the third level is a mixture of $3s\ ^2S_{\frac{1}{2}}$, $3p\ ^2P_{\frac{1}{2}}\ ^2P_{\frac{3}{2}}$, $3d\ ^2D_{\frac{3}{2}}\ ^2D_{\frac{5}{2}}$, etc. Of course, for any one atom only one of these possibilities exists at one time, but as there are always many atoms present all the possibilities may be considered at once. The series of transitions from the levels $n = 2, 3, 4$, etc., to the lowest one where $n = 1$ gives the Lyman series in the ultra-violet; the Balmer series arises from the transitions to the second level, $n = 2$, from those still higher, while the infra-red series are due to inward transitions to the third, fourth, and fifth levels, respectively. Apparatus of very high resolving power shows, however, that the hydrogen lines are really very close multiplets, indicating that the coalescence of the terms is not as exact as has been stated above.

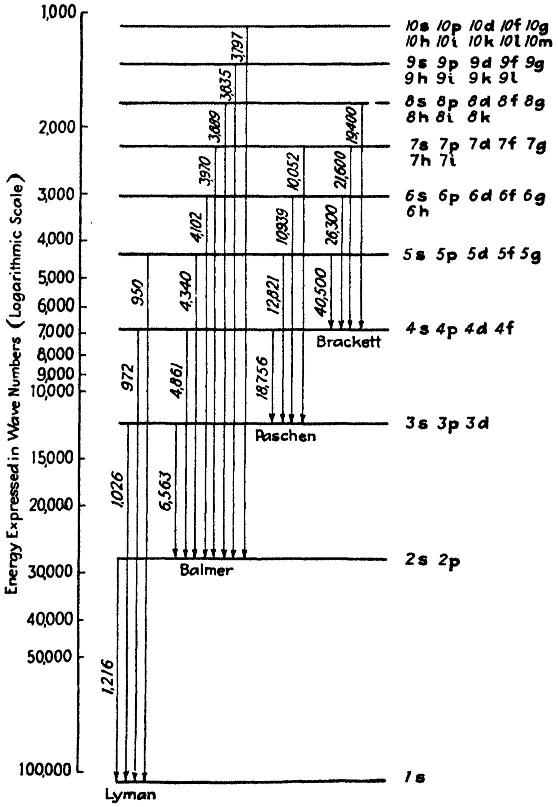

FIG. 7-11.—Hydrogen energy levels. The ordinates are the wave numbers, which are proportional to the energies of the levels, plotted on a logarithmic scale for convenience. The zero is taken at the ion. Transitions are indicated by vertical lines; the corresponding wave lengths in Ångströms are given beside them. Electron structures are shown on the right.

Relativity in conjunction with the electron spin suffices to explain the slight separation of the levels.

LOW HYDROGEN TERMS[1]

Energy in wave-number units, measured from the ion

1*s*	109,677.82	7*s* 7*p* 7*d*, etc.	2,238.33
2*s* 2*p*	27,419.51	8*s* 8*p* 8*d*, etc.	1,713.72
3*s* 3*p* 3*d*	12,186.46	9*s* 9*p* 9*d*, etc.	1,354.06
4*s* 4*p* 4*d*, etc.	6,854.88	10*s* 10*p* 10*d*, etc.	1,096.77
5*s* 5*p* 5*d*, etc.	4,387.13	11*s* 11*p* 11*d*, etc.	906.43
6*s* 6*p* 6*d*, etc.	3,046.62	12*s* 12*p* 12*d*, etc.	761.64

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[1] FOWLER, "Report on Series and Line Spectra," Fleetway Press (1922).

7-13. Experiment on the Sodium Spectrum.—The simplest source for the sodium yellow lines is a piece of asbestos washed in a sodium chloride solution and held in a Bunsen flame. This produces only the yellow lines with any appreciable intensity; a more violent source of excitation is required to bring out the rest of the spectrum. A very simple and adequate method is a carbon arc inoculated with sodium chloride or metallic sodium. The carbon electrodes, about the diameter of a lead pencil, are ground down to a rough point and a small hole is drilled in the end of each. Salt is put into these cavities, or better still a small pellet of metallic sodium is pushed into each. The arc should be run in a vertical position, with the positive pole below if direct current is available. A series rheostat limits the current to 2 or 3 amp. Carbon is particularly suitable as a holder since the line spectrum consists of but one line at 2478 Å in the whole range from the extreme red to 2000 Å. There is, however, an intense continuous spectrum given off by the incandescent solid and, to lesser extent, by the hot particles of carbon which fly off the electrodes into the arc. Hence it is desirable to make the spectroscope slit quite short and cast on it an image of the arc between the electrodes. The lens used for this purpose must be of quartz if it is desired to photograph the principal series. If such a lens is not available, the source is simply mounted a few inches in front of the slit. An exposure of about 1 sec. is sufficient to bring up the principal, sharp, and diffuse doublets in the yellow region with a small prism instrument and a panchromatic plate, but several seconds more are required to photograph the lines of shorter wave length. To prevent overexposure of the yellow lines a didymium filter, such as the Corning 512, may be placed in front of the slit during this part of the exposure. The spectrum photographed in this manner gives excellent reason for the historical phraseology "diffuse series"; the lines of this group are extremely fuzzy. Beautifully sharp lines in all the series may be obtained by using as a source a vacuum sodium arc. Strutt[1] has given a description of an arc which can be made very simply and which is easily demountable for cleaning and repair. As ordinary glass is attacked by hot sodium vapor, a sodium-resistant glass should be used if possible. Pyrex is not attacked so rapidly as some other glasses and may be rendered still more resistant by coating it with a layer of borax. This may be done by pouring a hot saturated solution of borax into the bulb, coating the walls thoroughly and decanting the excess liquid. The bulb may then be connected to a vacuum system to promote evaporation. When the borax is dry, the glass is heated nearly to its melting point, until the borax fuses and leaves a clear, smooth coating. Vacuum sodium arcs may be obtained commercially. For these arcs the didymium filter should be used for about 2 min. and a blue filter added for about 2 hr. to bring up the higher series members. Argon in the tube gives a strong set of lines below 4980 Å, so that the resultant picture exhibits the sodium series rather less strikingly.

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[1] STRUTT, *Proc. Roy. Soc.*, **96**, 272 (1919).

The sharp and diffuse series may be photographed with a glass instrument, but to obtain more than the first member of the principal series a quartz spectroscope must be used. For a few seconds a comparison spectrum of mercury is put on the plate with the slit a different length, and the wave numbers of the lines in the sodium series calculated by means of the Hartmann formula.

Sodium gives a typical example of a one-electron spectrum. The electron structure of the normal state is:

$$\begin{array}{cccc} 1s^2 & 2s^2 & 2p^6 & 3s \\ \uparrow & \uparrow & \uparrow & \\ \text{He} & \text{Be} & \text{Ne} & \end{array}$$

in which we see the completed shells of helium, beryllium and neon underlying the single $3s$ electron characteristic of sodium. By the vector-model theory we see that the closed shells may be neglected and that the $3s$ electron gives rise to a $^2S_{1/2}$ term. As the electron is raised to greater total quantum numbers but remaining of an s type, *i.e.*, through the series $4s$, $5s$, $6s$, $7s$, etc., we obtain a series of $^2S_{1/2}$ terms, until for ∞s the electron is completely removed leaving the sodium ion behind. For other than the normal state the electron may be of the p type, so that the various excited conditions $3p$, $4p$, $5p$, etc., form a series of pairs of levels, $^2P_{1/2}$, $^2P_{3/2}$. If the electron is of the d type we have the $3d$, $4d$, $5d$, etc., configurations yielding the series of level pairs $^2D_{3/2}$, $^2D_{5/2}$. These multiple levels are "regular," *i.e.*, the smaller J value goes with the lower term. We anticipate transitions from the ^2P terms to the ^2S and ^2D terms, but none between the latter two because of the L selection rule.

The sharp line series is composed of pairs of lines with a constant wave-number difference, for they are given by $3p\,^2P_{1/2} - ns\,^2S_{1/2}$ and $3p\,^2P_{3/2} - ns\,^2S_{1/2}$, where n increases by unit steps from the lowest value $n = 4$. In the Rydberg form this is written as

$$\tilde{\nu} = \frac{R}{(n' + \mu')^2} - \frac{R}{(n + \mu)^2}$$

where n increases for each member of the series, μ and n' are constants, and μ' can have either of two constant values; the fixed term is double.

The principal line series is made up of pairs of lines with a decreasing wave-number difference since they are given by $3s\,^2S_{1/2} - np\,^2P_{1/2}$ and $3s\,^2S_{1/2} - np\,^2P_{3/2}$, with n increasing through integral values, beginning at 3. The Rydberg expression is

$$\tilde{\nu} = \frac{R}{(n' + \mu')^2} - \frac{R}{(n + \mu)^2}$$

where n' and μ' are each constant, n increases by unit steps, and μ can have either of two constant values. The running term is double with the separation becoming less and less, for the two series of levels formed by the $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ terms converge together when the p electron has been completely removed.

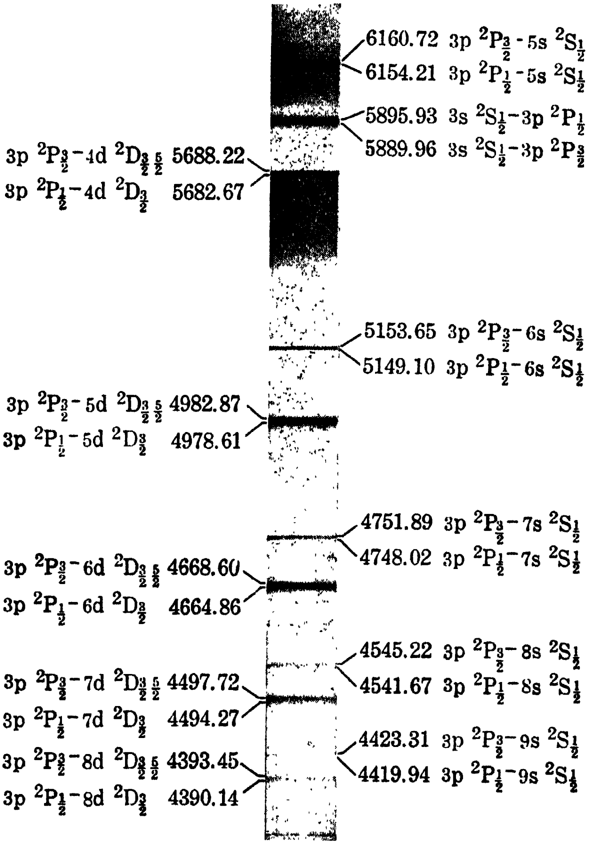
6160.72 $3p\ ^2P_{\frac{3}{2}} - 5s\ ^2S_{\frac{1}{2}}$
6154.21 $3p\ ^2P_{\frac{1}{2}} - 5s\ ^2S_{\frac{1}{2}}$
5895.93 $3s\ ^2S_{\frac{1}{2}} - 3p\ ^2P_{\frac{1}{2}}$
5889.96 $3s\ ^2S_{\frac{1}{2}} - 3p\ ^2P_{\frac{3}{2}}$
$3p\ ^2P_{\frac{3}{2}} - 4d\ ^2D_{\frac{3}{2}\frac{5}{2}}$ 5688.22
$3p\ ^2P_{\frac{1}{2}} - 4d\ ^2D_{\frac{3}{2}}$ 5682.67
5153.65 $3p\ ^2P_{\frac{3}{2}} - 6s\ ^2S_{\frac{1}{2}}$
5149.10 $3p\ ^2P_{\frac{1}{2}} - 6s\ ^2S_{\frac{1}{2}}$
$3p\ ^2P_{\frac{3}{2}} - 5d\ ^2D_{\frac{3}{2}\frac{5}{2}}$ 4982.87
$3p\ ^2P_{\frac{1}{2}} - 5d\ ^2D_{\frac{3}{2}}$ 4978.61
4751.89 $3p\ ^2P_{\frac{3}{2}} - 7s\ ^2S_{\frac{1}{2}}$
4748.02 $3p\ ^2P_{\frac{1}{2}} - 7s\ ^2S_{\frac{1}{2}}$
$3p\ ^2P_{\frac{3}{2}} - 6d\ ^2D_{\frac{3}{2}\frac{5}{2}}$ 4668.60
$3p\ ^2P_{\frac{1}{2}} - 6d\ ^2D_{\frac{3}{2}}$ 4664.86
4545.22 $3p\ ^2P_{\frac{3}{2}} - 8s\ ^2S_{\frac{1}{2}}$
4541.67 $3p\ ^2P_{\frac{1}{2}} - 8s\ ^2S_{\frac{1}{2}}$
$3p\ ^2P_{\frac{3}{2}} - 7d\ ^2D_{\frac{3}{2}\frac{5}{2}}$ 4497.72
$3p\ ^2P_{\frac{1}{2}} - 7d\ ^2D_{\frac{3}{2}}$ 4494.27
4423.31 $3p\ ^2P_{\frac{3}{2}} - 9s\ ^2S_{\frac{1}{2}}$
4419.94 $3p\ ^2P_{\frac{1}{2}} - 9s\ ^2S_{\frac{1}{2}}$
$3p\ ^2P_{\frac{3}{2}} - 8d\ ^2D_{\frac{3}{2}\frac{5}{2}}$ 4393.45
$3p\ ^2P_{\frac{1}{2}} - 8d\ ^2D_{\frac{3}{2}}$ 4390.14

FIG. 7-12.—The spectrum of sodium in the visible region, photographed with a small glass-prism instrument. The source was a carbon arc inoculated with metallic sodium. A didymium filter was used during part of the exposure. Several members of the sharp and diffuse and one member of the principal series are indicated.

The diffuse series is composed in a similar manner of triplet sets of lines. The fixed term has two components $3p\,^2P_{\frac{1}{2}}$ and $3p\,^2P_{\frac{3}{2}}$ while the running term is also double, $nd\ ^2D_{\frac{3}{2}}$ and $nd\ ^2D_{\frac{5}{2}}$, but only three out of the four possible combinations occur because of the J selection rule, *i.e.*, the combination $^2P_{\frac{1}{2}} - {}^2D_{\frac{5}{2}}$ is forbidden since J may not change by 2. Two of the lines maintain a constant wave number difference throughout the series due to the doubleness of the fixed term, while the third line closes in on the others as the separation of the two components of the running term becomes less. When the *d* electron is completely removed, the two ${}^2D$ levels coincide. (As a matter of fact the separation of the two levels of the ${}^2D$ term of sodium is so small that it has never been directly observed. The ${}^2P - {}^2D$ combinations are apparently pairs of lines with a constant wave-number difference.)

It is worth while noting why one would expect the pair of ${}^2P$ levels and the pair of ${}^2D$ levels, each to fuse together as the ionizing limit is reached. Whether the ion is formed by the removal of an electron characterized by the symbol *s*, *p*, or *d* the resulting electron configuration is the same, namely, the closed shell of neon. As we have seen, closed shells give rise only to a ${}^1S_0$ term. Hence the result of ionization must always be this single level, which condition the ${}^2P$ and ${}^2D$ levels approach in the limit. It should also be noted that we might expect to observe the "second" principal, sharp, and diffuse series which are the results of combinations with the fixed lower terms $4s\,{}^2S_{\frac{1}{2}}$, $4p\,{}^2P_{\frac{1}{2},\frac{3}{2}}$, and $4d\,{}^2D_{\frac{3}{2},\frac{5}{2}}$, respectively. These lines are, however, quite faint.

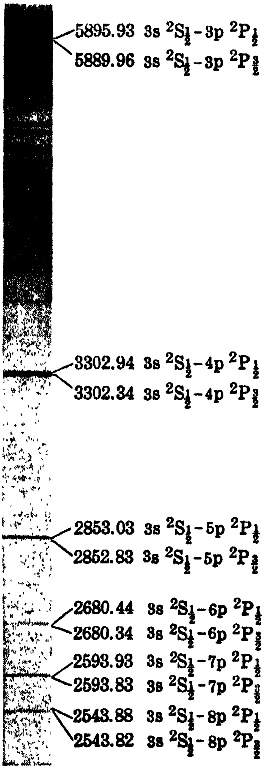
5895.93 $3s\ {}^2S_{\frac{1}{2}}-3p\ {}^2P_{\frac{1}{2}}$
5889.96 $3s\ {}^2S_{\frac{1}{2}}-3p\ {}^2P_{\frac{3}{2}}$
3302.94 $3s\ {}^2S_{\frac{1}{2}}-4p\ {}^2P_{\frac{1}{2}}$
3302.34 $3s\ {}^2S_{\frac{1}{2}}-4p\ {}^2P_{\frac{3}{2}}$
2853.03 $3s\ {}^2S_{\frac{1}{2}}-5p\ {}^2P_{\frac{1}{2}}$
2852.83 $3s\ {}^2S_{\frac{1}{2}}-5p\ {}^2P_{\frac{3}{2}}$
2680.44 $3s\ {}^2S_{\frac{1}{2}}-6p\ {}^2P_{\frac{1}{2}}$
2680.34 $3s\ {}^2S_{\frac{1}{2}}-6p\ {}^2P_{\frac{3}{2}}$
2593.93 $3s\ {}^2S_{\frac{1}{2}}-7p\ {}^2P_{\frac{1}{2}}$
2593.83 $3s\ {}^2S_{\frac{1}{2}}-7p\ {}^2P_{\frac{3}{2}}$
2543.88 $3s\ {}^2S_{\frac{1}{2}}-8p\ {}^2P_{\frac{1}{2}}$
2543.82 $3s\ {}^2S_{\frac{1}{2}}-8p\ {}^2P_{\frac{3}{2}}$

FIG. 7-13.—The spectrum of sodium in the visible and near ultraviolet, taken with a small quartz-prism instrument and an inoculated carbon arc. Six members of the principal series are shown.

The Grotrian diagram of the low energy levels of sodium is shown in Fig. 7-14; the zero energy is taken at the ion so all the levels have negative energies, the lowest level being the normal state of the atom. It is observed that the smallest energies that can be absorbed by the sodium atom in the normal state, $3s\,{}^2S_{\frac{1}{2}}$, raise it to the states $3p\,{}^2P_{\frac{1}{2},\frac{3}{2}}$. These upward transitions correspond to the absorption of energy equal to that emitted in the two yellow lines 5889 Å and 5895 Å. These lines are called the *resonance lines* of the atom by analogy with an oscillating mechanical system which is easily set into motion by a periodic force in resonance with the natural period of the system. These lines and the other members of the principal series are the only lines that can be absorbed by a sodium atom in the normal state. We shall refer again to this point in the following chapter.

The sodium terms obey a Ritz formula more accurately than a Rydberg one, but we may consider that the simpler Rydberg expression is adequate for the accuracy which can be attained with a small prism

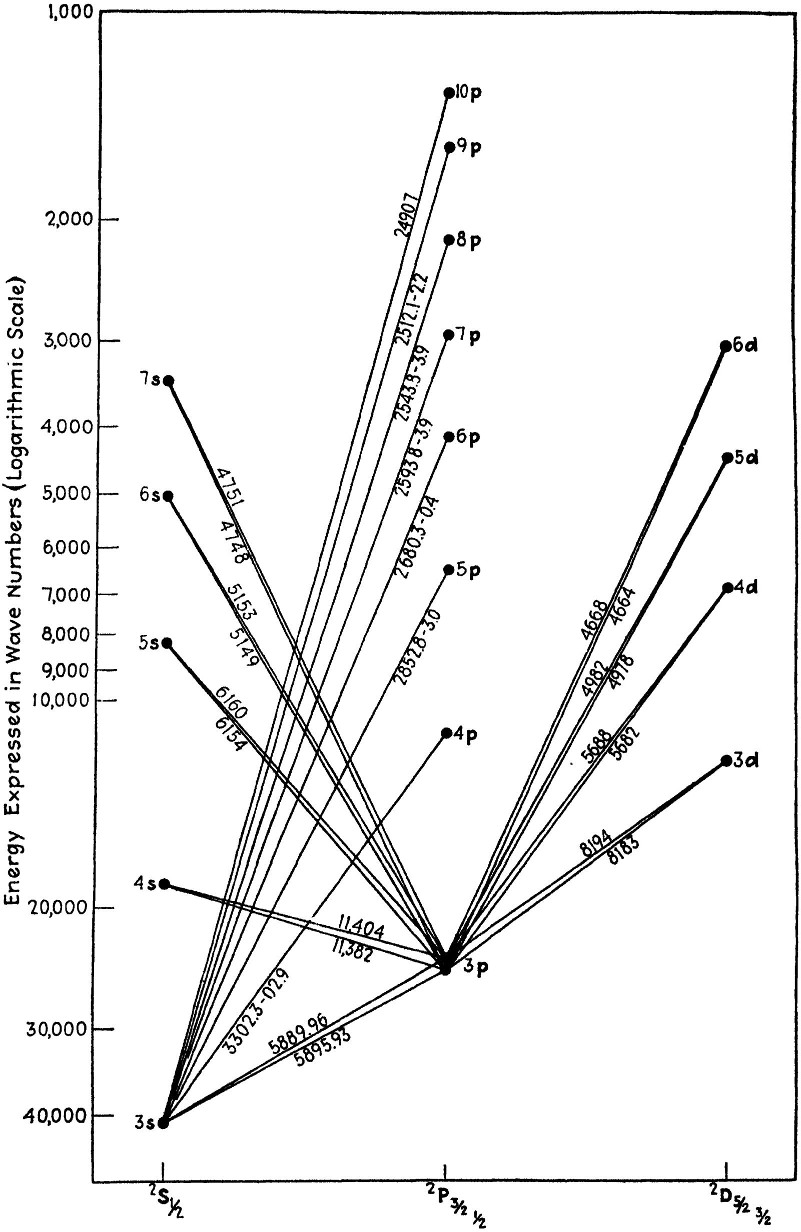

FIG. 7-14.—The Grotrian diagram of sodium. The energy levels are represented by dots, the electron configuration, outside the closed shells, being given alongside. The ^2P levels are all double but too close to show on this diagram, and the double ^2D levels are so close together that they have not been resolved. In a double level the one with the smaller J value is the lower. Wave lengths of the spectral lines are given on the diagonals, which represent transitions.

spectrograph. Any two successive lines of a series to which a Rydberg expression is applicable may be represented by

$$\tilde{\nu}_1 = L - T_1 \qquad \tilde{\nu}_2 = L - T_2$$

$$\tilde{\nu}_1 = L - \frac{R}{(n + \mu)^2} \qquad \tilde{\nu}_2 = L - \frac{R}{(n + 1 + \mu)^2}$$

where n is an integer and μ is a constant characteristic of the series. L is the unknown energy, expressed in wave numbers, of the lower fixed term measured from the ion as zero. T_1 and T_2 are the energies of two successive running terms, also measured from the ion. The difference of the wave numbers of the two lines is then the difference between the values of two successive terms

LOW SODIUM TERMS[1]
Energy in wave-number units measured from the ion

Configuration	Term $^2S_{\frac{1}{2}}$	Configuration	Term $^2P_{\frac{1}{2}\frac{3}{2}}$	Configuration	Term $^2D_{\frac{3}{2}\frac{5}{2}}$
3*s*	41,449.00	3*p*	24,492.83 24,475.65	3*d*	12,276.18
4*s*	15,709.50	4*p*	11,181.63 11,176.14	4*d*	6,900.35
5*s*	8,248.28	5*p*	6,408.83 6,406.34	5*d*	4,412.47
6*s*	5,077.31	6*p*	4,152.80 4,151.30	6*d*	3,061.92
7*s*	3,437.28	7*p*	2,908.93 2,907.46		
		8*p*	2,150.69 2,149.80		
		9*p*	1,655.31 1,654.08		
		10*p*	1,312.28		
		11*p*	1,065.86		

$$\tilde{\nu}_2 - \tilde{\nu}_1 = T_1 - T_2 = \frac{R}{(n + \mu)^2} - \frac{R}{(n + 1 + \mu)^2}$$

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[1] BACHER AND GOUDSMIT, "Atomic Energy States," McGraw-Hill (1932).

Tables[1] have been prepared giving values of the function $R/(n + \mu)^2$ for integral values of n from 1 to 10 and with μ in small steps from 0 to 1. Differences between the values of the function for successive values of n are also given. It is therefore only necessary to look among these differences for the value $\tilde{\nu}_2 - \tilde{\nu}_1$ (interpolating if necessary) to find in adjacent columns, characterized by a particular value of μ, the numerical values of the two terms T_1 and T_2. The limit L is then found from the relation

$$L = \tilde{\nu}_1 + T_1 = \tilde{\nu}_2 + T_2$$

The theoretical Rydberg values of the succeeding terms in the series may be found from the tables by taking the numbers given under successive values of n and the same value of μ as found before. These theoretical terms, T_3, T_4, T_5, etc., when subtracted from the limit L (just determined) give the theoretical values of the successive lines in the series, $\tilde{\nu}_3$, $\tilde{\nu}_4$, $\tilde{\nu}_5$, etc. The order of agreement of these values with those found from the plate measurement shows how accurately the particular series obeys a Rydberg formula. In general, a more accurate fit is obtained if the limit L is determined by applying the Rydberg equation to two of the higher members of the line series.

7-14. Experiment on the Mercury Spectrum.—The source of mercury radiation is most conveniently one of the commerciably obtainable glass or quartz arcs. The latter type is necessary if the ultra-violet spectrum is to be obtained. Alternatively one of the home-made mercury discharges or arcs, as described in Sects. **7-15** and **8-5** may be used. As the dispersion of a glass spectrograph is better in the visible region, it is advisable to use one of this type for the lines down as far as 4000 Å. The arc is focused on the slit of the spectroscope with a glass lens. Exposures of a few seconds suffice for most of the lines if a rapid panchromatic plate is used. The red lines may be brought up by an additional exposure of a few minutes with either of the Wratten filters A-25 or F-29. In the ultraviolet region the discharge tube, lens, and spectroscope train must all be of quartz. Again exposures of a few seconds suffice. The strong visible lines which were measured with a grating are used as standards, and the wave numbers of the weaker lines in the visible and the lines in the ultraviolet are calculated with a Hartmann formula.

Mercury gives an interesting example of a simple two-electron spectrum. The electron structure in the normal state consists of:

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[1] Fowler, "Report on Series and Line Spectra," Fleetway Press (1922).
Hicks, "Analysis of Spectra," Cambridge University Press (1922).
Paschen and Götze, "Seriengesetze der Linienspektren," Springer (1922).
Paschen, Sawyer, Mack, and Humphreys, *J. Optical Soc. Am.*, **16**, 231 (1928).
Bacher and Goudsmit "Atomic Energy States," p. 544, McGraw-Hill (1932).

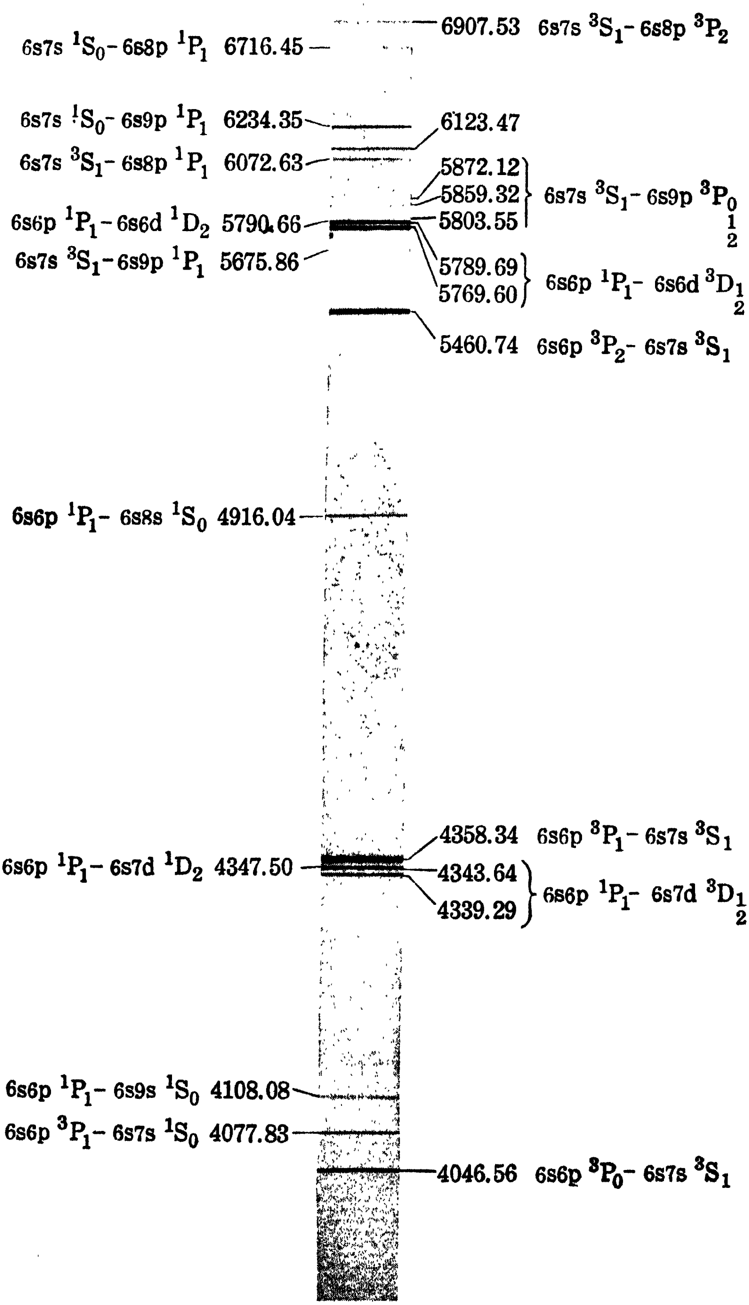
6907.53 6s7s $^3S_1$- 6s8p $^3P_2$
6s7s $^1S_0$- 6s8p $^1P_1$ 6716.45
6s7s $^1S_0$- 6s9p $^1P_1$ 6234.35
6123.47
6s7s $^3S_1$- 6s8p $^1P_1$ 6072.63
5872.12
5859.32
5803.55
6s7s $^3S_1$- 6s9p $^3P_0$ 1 2
6s6p $^1P_1$ - 6s6d $^1D_2$ 5790.66
6s7s $^3S_1$- 6s9p $^1P_1$ 5675.86
5789.69
5769.60
6s6p $^1P_1$- 6s6d $^3D_1$ 2
5460.74 6s6p $^3P_2$- 6s7s $^3S_1$
6s6p $^1P_1$- 6s8s $^1S_0$ 4916.04
4358.34 6s6p $^3P_1$- 6s7s $^3S_1$
6s6p $^1P_1$- 6s7d $^1D_2$ 4347.50
4343.64
4339.29
6s6p $^1P_1$- 6s7d $^3D_1$ 2
6s6p $^1P_1$- 6s9s $^1S_0$ 4108.08
6s6p $^3P_1$- 6s7s $^1S_0$ 4077.83
4046.56 6s6p $^3P_0$- 6s7s $^3S_1$

Fig. 7-15.—The spectrum of mercury in the visible region, taken with a small glass instrument and a vacuum arc, as described in the text.

$$\underset{\text{He}}{\underset{\uparrow}{1s^2}}\quad \underset{\text{Ne}}{\underset{\uparrow}{2s^2\,2p^6}}\quad \underset{\text{A}}{\underset{\uparrow}{3s^2\,3p^6}}\quad \underset{\text{Kr}}{\underset{\uparrow}{3d^{10}\,4s^2\,4p^6}}\quad \underset{\text{Xe}}{\underset{\uparrow}{4d^{10}\,5s^2\,5p^6}}\quad 4f^{14}\,5d^{10}\,6s^2$$

All of these are completed shells so that the normal state is a $^1S_0$. The

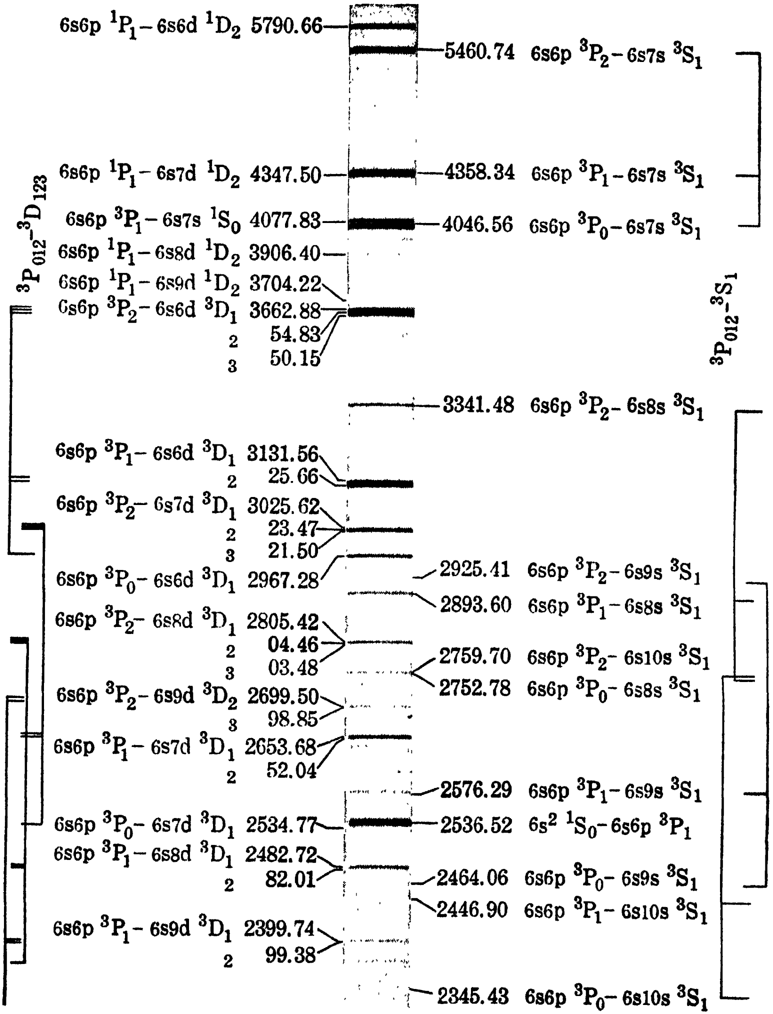

FIG. 7-16.—The spectrum of mercury in the visible and near ultra-violet, taken with a small quartz prism instrument and a quartz vacuum arc. Two of the series of multiplets are indicated.

higher or excited levels are occupied when one of the 6s electrons is raised to a more energetic state. In this case all but these two electrons are in closed shells, so that the expression "two-electron spectrum" is understandable. The configuration 6*s* 6*p* according to the vector model forms the levels $^3P_{2,1,0}$ and $^1P_1$; further excitation of the *p* electron to the 7*p*, 8*p*, 9*p*, etc., states gives rise to the series of higher ^3P and ^1P levels. The structures 6*s*7*s*, 6*s*8*s*, 6*s*9*s*, etc., form the series of levels $^3S_1$ and $^1S_0$, while 6*s*6*d*, 6*s*7*d*, 6*s*8*d*, etc., give the series of $^3D_{3,2,1}$ and $^1D_2$ terms. The *l*-sum rule permits combinations between the even (*S* and *D*) and odd (*P*) terms. We see from the Grotrian diagram that combinations occur not only within the singlet and triplet systems, from ^1S to ^1P, ^1D to ^1P, ^3S to ^3P, and ^3D to ^3P, but also that intersystem jumps occur from ^1S to ^3P and from ^3D to ^1P; these are sometimes called intercombination lines. The multiplets are said to be regular as the small *J*'s go with the low levels.

Whereas in sodium the several lines due to combinations between the various levels of two multiplets are very close together, in mercury they are often quite far apart. The close pairs of lines from the combinations $^1P_1 - {}^3D_1$ and $^1P_1 - {}^3D_2$ can be seen for two members of the series in the accompanying photograph; the three lines due to $^3S_1 - {}^3P_0$, $^3S_1 - {}^3P_1$, and $^3S_1 - {}^3P_2$, showing wider separations are also visible in Fig. 7-15. Examples of multiplets for which the relationship is not visible at first sight but comes only from a detailed analysis of the spectrum are given by the combinations $^3P_{2,1,0} - {}^3S_1$ and $^3P_{2,1,0} - {}^3D_{3,2,1}$. In the first case not only are the three lines of each multiplet widely separated, but several members of the series overlap; in the second case the multiplets are each composed of six lines in close groups of three, two, and one; here again the successive members of the series overlap.

It is often convenient to express energies given in wave numbers in terms of equivalent electron volts, or the potential through which an electron would have to fall in order to acquire the given energy. This may be done through the relation

$$h\nu = hc\tilde{\nu} = \frac{eV}{300}$$

$$\tilde{\nu} = \frac{eV}{300hc}$$

$$\tilde{\nu} = 8{,}106\ V$$

where the potential is in volts and the wave number in cm^{-1}.

The resonance line, $6s^2\ ^1S_0 - 6s6p\ ^3P_1$, has a wave length of 2536 Å, corresponding to 4.86 electron volts. The *J* selection principle ($\Delta J = \pm 1$ or 0 with the change $J = 0$ to $J = 0$ excluded) forbids the absorption transitions from the low $^1S_0$ state to either of the companion levels 6*s*6*p* $^3P_2$ or $^3P_0$. The second resonance line, $6s^2\ ^1S_0 - 6s6p\ ^1P_1$, is at 1849 Å, which corresponds to 6.67 electron volts. Hence if the normal atom be supplied with energy ranging from zero to something less than 6.67 volts, only that part of it equal to 4.86 volts can be absorbed and only the 2536 line will be subsequently emitted. It should also be noted that if the atoms are left at the end of some process in the $^3P_{2,1,0}$ energy states only those atoms in the $^3P_1$ state can return to the normal level with the emission of radiation. There are no possible ways for the $^3P_{2,0}$ levels to become emptied by radiation from the atoms because

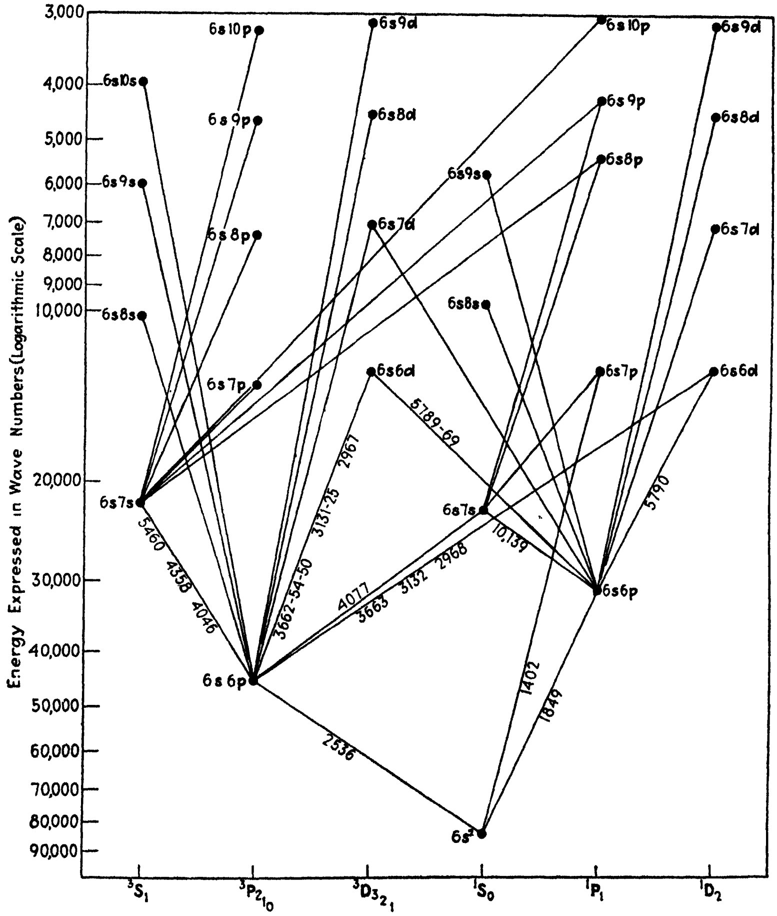

FIG. 7-17.—The Grotrian diagram of mercury. The ^3P and ^3D levels are all triple; the dots represent the center of gravity. In a set of multiple levels the J value decreases downward. For a more detailed diagram of the lower levels see Fig. 8-3.

of the J selection rule. These two levels are therefore called *metastable* because they remain occupied until their energy is drained away as kinetic energy or energy of excitation upon collision with the walls of the tube or with other atoms or molecules. As a consequence these levels are occupied for a much longer time than are the ordinary excited levels. We shall return to these points in Chap. VIII.

LOW MERCURY TERMS[1]
Energy in wave-number units measured from the ion

Configuration	Term $^3S_1$	Configuration	Term $^3P_{\substack{0\\1\\2}}$	Configuration	Term $^3D_{\substack{1\\2\\3}}$
6*s* 7*s*	21,830.8	6*s* 6*p*	46,536.2	6*s* 6*d*	12,845.1
			44,768.9		12,785.0
6*s* 8*s*	10,219.9		40,138.3		12,749.9
6*s* 9*s*	5,964.7	6*s* 7*p*	14,664.6	6*s* 7*d*	7,096.5
			14,519.1		7,073.2
6*s* 10*s*	3,912.8		12,973.5		7,051.7
		6*s* 8*p*	7,734.6	6*s* 8*d*	4,502.7
			7,714.4		4,491.0
	$^1S_0$		7,357.8		4,478.7
6*s*^{2}	84,178.5	6*s* 9*p*	4,805.8	6*s* 9*d*	3,110.2
			4,768.7		3,104.5
6*s* 7*s*	20,253.1		4,604.7		3,096.3
6*s* 8*s*	9,776.9	6*s* 10*p*	3,279.6		$^1D_2$
			3,264.7		
6*s* 9*s*	5,777.4		3,158.4	6*s* 6*d*	12,848.3
			$^1P_1$	6*s* 7*d*	7,117.5
		6*s* 6*p*	30,112.8	6*s* 8*d*	4,521.0
		6*s* 7*p*	12,886.1	6*s* 9*d*	3,124.2
		6*s* 8*p*	5,368.2		
		6*s* 9*p*	4,217.3		
		6*s* 10*p*	3,027.0		

7-15. Experiment on the Zeeman Effect.—A brief calculation shows that the Zeeman effect cannot be observed except with spectroscopic apparatus of high resolving power, at least with magnetic fields that can be produced readily. As $\lambda = 1/\tilde{\nu}$, $\Delta\lambda = -\Delta\tilde{\nu}/\tilde{\nu}^2 = -\lambda^2\Delta\tilde{\nu}$, and since the Lorentz separation for unit field is $\Delta\tilde{\nu} = 4.674 \times 10^{-5}$ cm.$^{-1}$ per gauss, we have $\Delta\lambda = 1.7 \times 10^{-5}$ Å per gauss at 6000 Å and $\Delta\lambda = 0.4 \times 10^{-5}$ Å per gauss at 3000 Å. The large electromagnets used in spectroscopic research give about 40,000 gauss, so that $\Delta\lambda = 0.68$ and 0.16 Å, respectively, at these two wave-length limits. The magnets generally available in lecture-room equipment give fields of about 10,000 gauss or less so that $\Delta\lambda$ is about 0.17 and 0.04 at these limits for a Zeeman pattern of one Lorentz unit, which is the order of magnitude generally found. The resolving power of a prism is given by $\frac{\lambda}{\Delta\lambda} = t\frac{dn}{d\lambda}$, where $\Delta\lambda$ is the wave-length difference that can just be resolved, t is the thickness of the base of the prism, and n is the index of refraction. For dense flint glass this means a thickness of about 6 cm. to resolve lines separated by 1 Å at 6000 Å, so that the ordinary small prism instrument is out of the question. The resolving power of a grating is equal to the product of the total number of lines and the order used. Good original gratings are expensive and replicas cannot be used with much success beyond the second order, so that a 2-in. replica grating containing, say, 30,000 lines could theoretically resolve lines separated by 0 1 Å at 6000 Å in the second order. A Zeeman separation of one Lorentz unit, with 10,000 gauss in the red end of the spectrum, might possibly just be detectable with such a grating, but it would scarcely be subject to quantitative measurement. It must be recalled that resolving powers are calculated on Rayleigh's definition of the term: Two lines of equal intensity are said to be resolved if the first diffraction minimum of one line lies at the central maximum of the other. This gives, to a first approximation, the resolving power to be expected from any optical arrangement. Lines have been observed as separate which are not resolvable in accordance with this definition, but it gives the order of magnitude of the resolution to be expected.

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[1] BACHER AND GOUDSMIT, "Atomic Energy States," McGraw-Hill (1932).

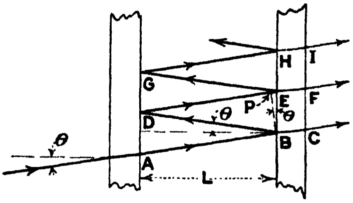

Fig. 7-18.—A diagram of the Fabry-Perot interferometer.

The simple Zeeman effect can, however, be easily measured with a small prism instrument in conjunction with a Fabry-Perot interferometer. Fixed-separation types of this instrument are relatively inexpensive and quite adequate for the purpose. We shall content outselves with only as much of the theory as is necessary for the present discussion. This type of interferometer consists of two accurately plane parallel plates of glass separated by a distance L and coated with a deposit of silver or other highly reflecting substance on their inner surfaces. If parallel monochromatic light strikes these plates at a small incidence angle θ, as in Fig. 7-18, part of the beam emerges at C and part is reflected at B back to D. Further partial reflection and transmission at each semi-silvered surface results in a group of beams emerging from the right-hand plate, apparently originating from the line of sources, A, D, G, etc. The path difference between adjacent beams, δ, is given by the following considerations:

$$\begin{aligned}\delta &= BD + DP = BD + DE - PE = 2BD - BE \sin\theta \\ &= \frac{2L}{\cos\theta} - 2L \tan\theta \sin\theta = \frac{2L}{\cos\theta}(1 - \sin^2\theta) \\ &= 2L\cos\theta\end{aligned}$$

If θ is such that $2L \cos\theta = n\lambda$, where n is an integer, the rays which emerge at this angle and are brought together by a lens interfere constructively, and a bright region results. In practice the rays of light falling on the plate are never exactly parallel to each other as they come from an extended source; in the case of an interferometer in a spectroscope train, the source is the entrance slit of the instrument. We may therefore at first consider the light to be incident on the plates at all angles in a solid cone. For the particular conical shell of semi-apex angle θ, the region of interference of the wave length λ is a circle in the focal plane of the lens, of order n. For a conical shell of slightly larger angle θ', the interference pattern is a larger circle of order $n - 1$. Every color therefore gives rise to a series of concentric circles. If a prism is introduced after the interferometer, the circles of the different colors are displaced so that they are no longer concentric. The use of a narrow entrance slit limits the field of view to a chord or diameter of these circles depending on the adjustment of the instrument. The pattern of a line spectrum resembles an ordinary spectrum except that each line is replaced by a series of dots (the intersections of the slit image with the circular patterns). A very small wave-length change in the light from the source causes the spots to move up or down, since for a given order $\cos\theta$ varies with λ. Only for relatively large wave-length changes can any lateral motion of the spots due to the dispersion of the prism be detected.

The interferometer is most conveniently mounted between the collimating lens and the prism of a photographic spectroscope. The plates are pressed together by three springs, controlled by screws, against three quartz separators of equal length; three carefully selected ball bearings may be used satisfactorily. The approximate separation is given by the manufacturers, or it can be measured with a good pair of calipers. Tightening the screws against the elasticity of the separators permits adjustment to exact parallelism; two other screws allow motion of the interferometer as a whole about vertical and horizontal axes perpendicular to the axis of the collimator. Adjustment is accomplished by trial and error until the dots appear as sharp as possible when viewed with a lens held behind the opening for the plate holder. A rather wide slit should be used, and it is desirable that the dots representing the intersections of the slit images with the interference circles lie along a diameter of these circles rather than along a chord. Due to the lower reflecting power of the silver coatings for the violet end of the spectrum, the number of contributing reflections, and hence the resolving power, falls off with decreasing wave length. Also, for a given setting of the plates, there are more orders visible in the short wave-length region so that the dispersion of the orders is less there, hence it is desirable to work in the long wavelength region if possible. The apparent sharpness of the spots increases away from the center of the pattern, but their separation also becomes less. It is most convenient, therefore, to effect a compromise by working with the rings, say between the fifth and the tenth, from the center of the pattern.

A source of mercury radiation which has been used satisfactorily for this experiment will be briefly described. To obtain as large a magnetic field as possible it is necessary to have the pole pieces of the magnet close together; hence a capillary discharge tube should be used. The electrodes, nickel cylinders welded to tungsten rods, are in bulbs outside the region of the pole pieces. Pyrex glass is essential, as soft glass is likely to break under the heat developed. The tube should be baked for several hours at about 400° C. and the electrodes heated with an induction furnace, if one is available, while the tube is on the pumping system. Alternatively, neon may be admitted at a pressure of a few millimeters and a discharge run for about an hour to remove, at least partially, undesirable impurities from the electrodes and the walls of the tube; this gas is then pumped out. A small amount of mercury is introduced and a few centimeters of neon; the tube is then sealed off. The neon greatly facilitates the running of the tube in a strong magnetic field, and practically no spectrum but that of mercury is observed at high current densities. The tube may also be used for measuring the Zeeman separations for the strong neon lines in the red if it is run with smaller currents. A small 10,000-volt transformer is an adequate power supply. A rheostat in the primary permits adjustment of the current; trial will show at what currents the discharge is most satisfactory. Occasional shaking to drive the mercury into the upper bulb is often helpful if the neon spectrum begins to appear. A lens is used to focus an image of the capillary between the pole pieces on the slit of the spectrograph.

Although the magnetic field may be increased by using wedge-shaped pole pieces to concentrate the lines of force near the capillary tube, the procedure is undesirable for the present purpose where an absolute determination of the field is to be made. Flat pole pieces produce a more uniform field into which a small search coil connected to a fluxmeter or ballistic galvanometer may be introduced. The coil should have an area small enough so that it can completely enter the region between the pole pieces when the discharge tube is in place, and it should have as large a number of turns as possible in order to obtain large throws. The number of maxwells, or total number of lines of force, indicated by the calibrated fluxmeter, is divided by the product of the area and the number of turns of the search coil to give the number of lines per square centimeter or the strength of the field in gauss. The theory of the fluxmeter or ballistic galvanometer may be found in many books on electrical instruments, such as those of Terry[1] or Smythe and Michels.[2] The magnet is quite likely to retain several hundred gauss of residual magnetism after the energizing circuit has been opened. Hence before taking the zero-field picture a rather weak current should be sent through the coils in the reverse direction until the fluxmeter indicates a vanishingly small residual field. A series of pictures are then taken with increasing field strengths up to the maximum of which the magnet is capable; care being taken to see that the plate holder is moved an adequate amount between each exposure.

Due to the closeness on the photographic plate of the different orders, it is not easy to distinguish the several additional spots produced by the anomalous Zeeman effect, so it is feasible to examine quantitatively only the simple type of pattern such as is produced by the combination between two singlet terms. We have seen that for such a line the pattern should consist of the original wave length accompanied by a satellite on either side, distant one Lorentz unit from the parent line for a field of 1 gauss. The singlet lines of the mercury spectrum are well suited for this experiment, and for the reasons given above those at the long wave-length end of the spectrum are the most convenient to use. The line 6,234.35 ($6s7s\ {}^1S_0 - 6s9p\ {}^1P_1$) would be excellent except that long exposures with red-sensitive plates are required, and the presence of neon lines might confuse the picture. The yellow line 5,790.66 ($6s6p\ {}^1P_1 - 6s6d\ {}^1D_2$) is well suited; it is almost coincident with 5,789.69 ($6s6p\ {}^1P_1 - 6s6d\ {}^3D_1$), but this line is very faint and does not appear with any appreciable intensity in the short exposures required.

Figure 7-19 shows the pictures obtained with a series of 20-sec. exposures at varying field strengths. At zero field the pattern is a series of dots given by the various orders. As the field increases, "wings" grow out from each order and finally become separated as distinct dots, thus showing that high- and low-frequency companion lines are developed. It is possible to compute the accurate wave lengths corresponding to every dot shown, provided the accurate wave lengths of three lines in the vicinity are known, but the process is rather laborious. We shall use an approximate method which is, however, capable of sufficient accuracy to determine the Zeeman separations to within a few per cent.

The positions of each dot on each pattern of the line 5790 are measured with a traveling microscope to 0.001 mm. if possible, and the results plotted against the measured field strength as shown in Fig. 7-20. Straight lines are drawn through the points representing the Zeeman components, and these are used to determine the field strength at which the Zeeman component of λ in the order $n + 1$ has been shifted to the position of the nth order of λ. Extrapolation of the lines may be resorted to if the largest available field is not sufficient to make the Zeeman component shift by one order. An average value of this field, H_1, is found

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[1] TERRY, "Advanced Laboratory Practice in Electricity and Magnetism," McGraw-Hill (1929).

[2] SMYTHE and MICHELS, "Advanced Electrical Measurements," Van Nostrand (1932).

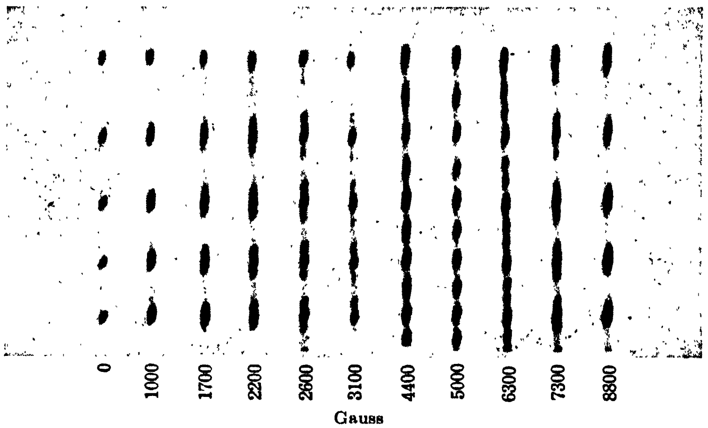

FIG. 7-19.—The interferometer patterns of the singlet mercury line, λ = 5790.66 Å, for a series of values of the magnetic field at the source.

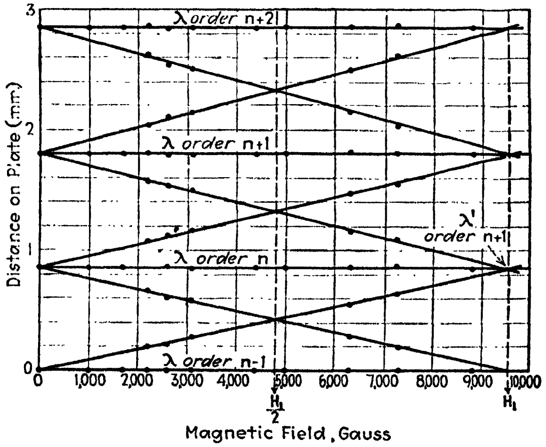

FIG. 7-20.—A plot of the interferometer patterns against the magnetic field strength, in the determination of the Zeeman separation of the mercury line 5790.66 Å.

from the behavior of each order visible. It should be observed that this field is just twice that at which the long and short wave-length components of two adjacent orders intersect.

We have in general that $n\lambda = 2L \cos \theta$ as the criterion for constructive interference, or, since θ is very small, $n\lambda = 2L$ approximately. Hence for the field H_1 at which the Zeeman component λ' of order $n + 1$ has moved into coincidence with the nth order of the original line λ, we have

$$n\lambda = (n + 1)\lambda'$$

hence

$$\lambda' - \lambda = \frac{n}{(n + 1)}\lambda - \lambda$$

or

$$\Delta\lambda = -\frac{\lambda}{n + 1}$$

We do not know the exact value of the order n, but we know that it is given approximately by $n = 2L/\lambda$. Hence for a plate separation of 1 or 2 cm. and $\lambda = 5790$ Å, n is of the order of 10^4. We certainly may neglect unity in comparison with this and write

$$\Delta\lambda = -\frac{\lambda}{n}$$

As $\tilde{\nu} = 1/\lambda$, where $\tilde{\nu}$ is the wave number, we have

$$\Delta\tilde{\nu} = -\frac{\Delta\lambda}{\lambda^2} = \frac{1}{n\lambda} = \frac{1}{2L}$$

This is the expression for the wave-number change due to the field H_1, and therefore the Zeeman separation for unit field is

$$\frac{\Delta\tilde{\nu}}{H_1} = \frac{1}{2LH_1}$$

where L is the separation of the interferometer plates, and H_1 is the field required to give a Zeeman separation equivalent to a shift of one order for the parent line. This quantity $1/2LH_1$ should theoretically be equal to the Lorentz unit, $e/4\pi m = 4.674 \times 10^{-5}$ cm.$^{-1}$. An accuracy of a few per cent may be expected. From this standpoint the experiment verifies the theory of the Zeeman effect and identifies the line 5,790 as being a singlet-singlet combination. Or, if the theory is assumed to be correct, the result may be taken as a measurement of the quantity e/m, the ratio of the charge to the mass of an electron in an atomic system

CHAPTER VIII

ATOMIC ENERGY STATES

8-1. Introduction.—When considered as a whole the preceding chapter may be regarded as an exposition of how the multitude of spectroscopic lines emitted by an element may be described systematically by the introduction of the concept of stationary energy states. Though these states, represented by spectroscopic terms, are called stationary, the great majority of them are far from stable, and an atomic system remains in an ordinary excited state only a very small fraction of a second. When the atom changes from one of these characteristic configurations to another of lower energy content the excess energy is radiated in accordance with the expression

$$h\nu = E_2 - E_1$$

The *ad hoc* characteristic of the assumptions made in the development of the preceding theory is greatly diminished by the completeness and consistency of the final scheme, and by its theoretical derivation, either on the old quantum theory with its highly arbitrary rules or on the more satisfactory and consistent methods of modern quantum mechanics. Nevertheless a great deal more confidence will be felt in the theory if further experimental evidence can be found to substantiate the predictions and consequences of the stationary state concept when applied to the explanation of phenomena other than those for which it was originally developed.

A large number of corroborative experiments suggest themselves. Under the ordinary conditions of exciting the spectrum of an element, such as in flames, arcs, or sparks, the atoms are subjected to a very heterogeneous supply of energy, *e.g.*, collisions with neutral atoms and molecules, ions, electrons, excited atoms, and photons. All these sources are often present and contribute in varying degrees to the phenomena observed, namely, the spectrum emitted and the positively and negatively charged particles which appear. More information as to the individual atomic processes may be gained by simplifying the mechanism of excitation and studying the effects of these different processes separately. In the subsequent sections we shall confine ourselves to a consideration of the simpler phenomena connected with the transfer of energy to atomic systems from radiation and from rapidly moving electrons, *i.e.*, by photon or electron bombardment.

Upon our previous theory we might expect the following processes to occur. The photon, if it contains the proper energy, may be completely absorbed and the atom raised to an excited state. After being excited it may radiate, or it may dispose of its energy of excitation by transferring it to another particle at a collision. As a second possibility, if the photon has sufficient energy to ionize the atom, it may be absorbed and an electron ejected. The energy of the ion may then be released by the recapture of an electron and radiation of the so-called recombination spectrum lying beyond the series limit, or it may be transferred to another particle, in the body of the vapor or on a surface, by some non-radiative process at which an electron is acquired by the ion. Third, the photon may be partially absorbed resulting in excitation; the unabsorbed fraction emerging from the process as radiation of an altered wave length. This is known as the *Raman effect.* The fourth possibility is that the photon is partially absorbed and the atom ionized, in which case a photon of altered wave length and an electron both leave the atom after the process. This is known as the *Compton effect.*

If the collision occurs between an electron and an atom there can be no total absorption of the electron, if we neglect the infrequent phenomenon of capture which results in the formation of a negative ion. Thus, by analogy with the third case, we may have the kinetic energy of the electron transferred as a whole or in part to the atom, producing excitation, the electron emerging from the process with a reduced velocity. If the electron has sufficient energy it may ionize the atom resulting in the production of two electrons and a positive ion, the excess kinetic energy of the impinging electron being shared in some way between the two electrons and the ion.

8-2. Experiments on Selective Absorption.—The explanation of the dark lines in the solar spectrum observed by Fraunhofer was first given by Kirchhoff: "The spectrum of every incandescent gas must be reversed, when it is penetrated by the rays of a source of light of sufficient intensity giving a continuous spectrum." That is, the light reaching us from the sun has traversed enormous distances through the surrounding vapors which have absorbed certain characteristic frequencies, and as a consequence the positions these would have occupied in a spectrum appear black in contrast to the intense continuous radiation on either side. The most familiar laboratory demonstration of this phenomenon is to pass "white" light from an arc or incandescent lamp through a vapor such as that of sodium and to observe that in this case, for instance, the continuous spectrum of the source is crossed by two relatively black lines at the precise wave-length positions of the yellow emission lines of sodium.

Modern atomic theory indicates that Kirchhoff's explanation needs a slight restriction. Only those colors are absorbed which are emitted when the atom returns from an excited state to the state in which it exists when the absorption process occurs. If the atoms are originally in the normal state, they are only capable of absorbing those frequencies corresponding to transitions from excited states to the normal state; other characteristic frequencies of the spectrum are not absorbed. A glance at the Grotrian diagram of sodium shows that the normal state is $3s\,^2S_{\frac{1}{2}}$; the only emission lines ending on this state are those of the principal series, due to jumps from the higher ^2P levels. These are the only lines which are absorbed when continuous radiation is passed through unexcited sodium vapor. For the sharp and diffuse series to be appreciably absorbed would require the presence of a large number of atoms in the $3p\,^2P$ states. It is true that these levels do become occupied every time the yellow lines 5890 and 5896 are absorbed, but it is known that the life time of such an excited state is only about 10^{-8} sec., after which the excitation energy is drained away by the emission of these same lines. Hence the ^2P levels are emptied almost as rapidly as they are filled, and the chance is extremely small that the atom should collide with a quantum of the requisite energy to lift it to any of the higher ^2S or ^2D levels during this short interval. The question may arise as to why the yellow lines actually appear to be absorbed if they are immediately reemitted. The reason is that the reemission takes place at random and only occasionally does the emitted photon travel in the direction of the photon that was absorbed. As this is the direction in which the observations are made, a net decrease in the intensity is observed owing to these absorption and reemission processes.

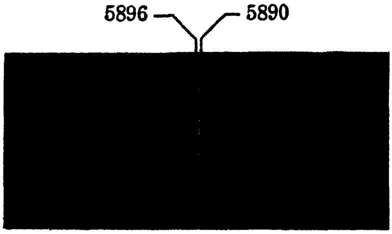

FIG. 8-1.—A photograph taken with a small glass spectroscope showing the absorption, from the continuous spectrum of an incandescent lamp, of the resonance lines by sodium vapor.

The absorption of the first principal series doublet, as in Fig. 8-1, may be observed by passing the continuous radiation from a carbon arc or an incandescent lamp through a glass tube containing sodium vapor and then into a small spectroscope. A Pyrex tube about 1 in. in diameter and 18 in. long, with clear ends, is satisfactory. It is evacuated in the usual manner and metallic sodium distilled into it by heating with a torch a small appendix containing a lump of the metal. The tube is then sealed off and wound with nichrome wire and asbestos to act as a furnace. To prevent the condensation of sodium on the ends, two 1-in. gaps should be left in the windings about 1 in. from each end; these gaps serve as cold guard rings. At a temperature of slightly over 300°C. the vapor pressure of sodium is sufficient to maintain an appreciable concentration of atoms in the light path, and the absorption becomes clearly visible. The vapor density may be increased by using higher temperatures, but unless the glass is resistant to the action of sodium vapor it is attacked fairly rapidly at much higher temperatures and rendered opaque. To observe the absorption of the higher series members in the ultra-violet, quartz windows and a quartz spectrograph must be used as well as a strong source of continuous radiation in this region such as an under-water spark or a strong hydrogen arc in a quartz tube. That the thermal agitation at the temperatures used is not sufficient to raise an appreciable number of atoms to excited states and thus possibly permit the absorption of lines other than those of the principal series is shown by the fact that the vapor is not self-luminous. In the sun, on the contrary, the heat is sufficient to keep many of the excited levels populated so that the absorption of lines of the other series is to be expected.

In a similar manner it can be shown that the light absorbed by unexcited mercury vapor corresponds to the transitions to higher states from the lowest level, $6s^2\ {}^1S_0$. The Grotrian diagram for this element shows that the absorption of light of wave length 2536 Å raises the atom to the $6s6p\ {}^3P_1$ state; this is the only absorption line in the easily accessible region of the spectrum. Other absorption possibilities are at 1849 and 1402 Å, corresponding to transitions from the normal state to $6s6p\ {}^1P_1$ and $6s7p\ {}^1P_1$ respectively; the first of these lies at the limit of transparency of quartz, and the second requires an evacuated fluorite or grating spectrograph, as air is opaque in that region. The demonstration of the absorption of the 2536 line by mercury vapor is not quite as simple as the corresponding experiment with sodium. It is desirable that the light absorbed should be part of a continuous spectrum so that any absorption is readily detected; if the light comes from a mercury arc, absorption is indicated merely by a reduction in intensity of the emitted 2536 line when the light passes through a cell containing mercury vapor, and this is far more difficult to observe. Ordinary carbon arcs and incandescent or Point-o-lite lamps are ruled out, as their intensity in the ultra-violet is very small, and in the case of the latter sources the thin glass wall completely cuts out the desired radiation. A condensed discharge through hydrogen in a quartz tube may be used as a source of continuous radiation in this region, but a different experimental arrangement altogether is equally permissible.

A very simple and satisfactory method is to use an under-water spark. If a violent discharge is maintained between electrodes under water, the arc has somewhat the characteristics of a miniature sun; due to the inertia of the surrounding water the metallic vapor arising from a rapid intense discharge is under great pressure and gives out an intense continuous spectrum throughout the visible and well below 2536 Å, as well as the line-spectrum characteristic of the material of the electrodes. Furthermore, the outer regions of the discharge are considerably cooler than the central core and hence contain many atoms in the normal state capable of absorbing their characteristic frequencies from the continuous spectrum emitted by the core. This corresponds very roughly to the absorption in the reversing layer of the sun, though in the latter case the temperature of the outer layer is still high enough to keep many atoms in highly excited states and the absorption of almost all of the spectral lines is observed.

In order to obtain a violent spark under water, a 25,000-volt transformer should be used with several Leyden jars in parallel shunted across the secondary; a capacity of about 0.005 μf. is satisfactory. The water gap and a sphere gap in air are placed in series across the transformer terminals. The purpose of the air gap is to prevent any flow of current through the water until the alternating potential has risen to a very high value at each cycle; both gaps then break down at once and the condensers discharge through the resulting low resistance with disruptive violence. The water vessel should be a strong glass beaker or a metal can of 1- or 2-liter volume with a quartz window waxed over a hole in the side. The joint should be made very solidly, or the mechanical shock transmitted through the water will blow the window out.

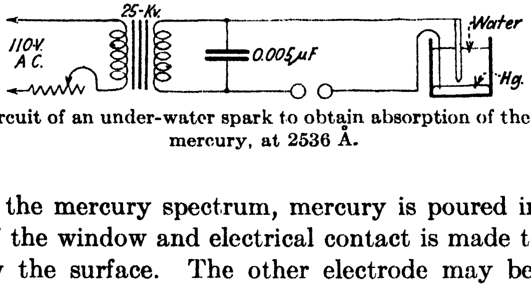

FIG. 8-2.—The circuit of an under-water spark to obtain absorption of the resonance line of mercury, at 2536 Å.

To obtain the mercury spectrum, mercury is poured into the vessel to the level of the window and electrical contact is made to it by a wire dipping below the surface. The other electrode may be a carbon or copper rod, terminating in a point, which is clamped rigidly in a vertical position so that there is a gap of 1 or 2 mm. between the point and the mercury surface. The external gap should have a separation of about 1 cm. Trial is necessary to obtain the best adjustment. Though the copper spectrum will appear if an electrode of this metal is used, it is more satisfactory than carbon as the latter is rapidly disintegrated. The water must be changed frequently as it becomes cloudy with colloidal particles; for exposures lasting more than a minute it is worth while to arrange for a continuous flow through the vessel. The arc is focused by means of a quartz lens on the slit of a small quartz spectrograph, and a photograph may be obtained with an exposure of about a minute.

8-3. Experiments on Resonance Radiation.—The preceding experiments have shown that the stationary state concept not only renders intelligible the emission spectra but also supplies a consistent explanation of the selective absorption of radiation by atoms initially in their normal states. The explanation involved the statement that when an atom absorbs energy, it very shortly thereafter returns to its normal state by reemission of radiation of the same frequency; absorption is observed because the reemitted light is directed at random and only occasionally is sent in the direction of the photon that was originally absorbed. The experiment now to be described is designed to verify this statement; *i.e.*, to observe this reemitted radiation of the same wave length as the original light but in a direction other than that of the original beam. Such emitted light is termed *resonance radiation* by analogy with a vibrating mechanical system.

We expect then, that if sodium vapor is illuminated with the wave lengths 5890 and 5896 Å, these and only these colors will be reradiated in all directions. The experimental verification of this prediction is quite simple. A resonance lamp in the usual shape of a straight portion terminated by a horn is prepared. This may be a Pyrex tube about 1 in. in diameter and 6 or 8 in. long. One end is sealed with a plane window or it may equally well be blown into a clear hemisphere; the other end is drawn into a cone and curved sideways to act as a light trap. A side tube leads to the pumps, and a small appendix containing several lumps of metallic sodium is sealed on to the tube. The tube should be torched for some minutes during evacuation to remove water vapor, then gentle heating of the appendix distills sodium into the tube where it condenses; the appendix may then be sealed from the tube and the tube itself sealed off the pumping system. It should then be painted with a dull black paint except over the end window and another clear space on one side to permit the entrance and exit of light. The tube is wrapped in asbestos and wound with nichrome heating wire and more asbestos, except over the two windows.

As the absorption is not to be observed, a light source giving a continuous spectrum is not necessary; great intensity of the sodium yellow lines is desired, however, so that a vacuum sodium arc should be used. For the excitation of all resonance spectra the incident light should be as close to the desired frequency as possible, as the word "resonance" implies. It is therefore desirable that the light source should not be surrounded by any absorbing layer of vapor with the consequent removal of the exact color it is desired to use. Such self-absorption, which is present to a certain extent in most light sources, is known as *self reversal.* A magnetic field applied to the light source may be used to force the discharge against one wall of the tube and squeeze out any absorbing layer on that side. Such a procedure is necessary if very strong resonance radiation is desired, but it has not been found necessary for the relatively simple experiments suggested in this chapter. For visual use, the light from a suitable source is directed by means of a lens through a small hole in a screen so that a narrow beam is sent down the length of the tube, and observation is made through the side window. A current is sent through the heating coil until a thermometer, whose bulb is included under the asbestos wrapping, reads about 110°C. The path of the beam is then seen as a brilliant yellow streak. For photographic recording with a spectroscope, greater intensity may frequently be obtained by illuminating the side window and directing the spectrograph down the length of the tube toward the curved horn. In either arrangement, if properly aligned, the intensity of the scattered light from the walls is very small.

An exposure of about a minute shows that only the yellow lines are reradiated. A test exposure with the tube cold shows no lines at all, proving that the light previously observed was not merely reflected from the walls. If a didymium glass filter, which strongly absorbs the yellow lines without appreciably reducing the intensity of the rest of the spectrum, is interposed between the source and the resonance lamp, the fluorescence disappears, showing that the yellow lines are necessary to cause the effect. Similarly filters that are transparent to the yellow but not to other colors may be used to show that the yellow light is sufficient. During the experiment it will be observed that sodium condenses slowly on the windows, but it can be removed by the gentle application of a Bunsen flame. At temperatures much above 120°C. the deposit forms with inconvenient rapidity; also, the absorption becomes so great that the exciting radiation cannot penetrate far into the tube but is limited to a region close to the entrance window.

A similar phenomenon can be observed with mercury vapor, although the effect is not so striking since the resonance radiation does not lie in the visible range. If the 2536 Å line from a quartz mercury arc is directed into an evacuated quartz tube containing pure mercury vapor, the same wave length is reemitted and may be detected with a quartz spectrograph. It is rather difficult to procure filters that will pass only the 2536 Å line so that the sufficiency of this monochromatic radiation is not easy to demonstrate; its necessity may be shown by interposing a sheet of glass, which is opaque to this wave length, between the source and resonance lamp and observing that the reemission ceases. It is not necessary to heat the resonance tube, as even at room temperature the vapor pressure of mercury is sufficient to maintain a large number of atoms in the path of the incident light. Details of the construction of a suitable tube are here omitted as the effect can be observed with a tube to be described presently for investigating a more complicated phenomenon. For convenience, a table of the vapor pressures of sodium and mercury through sufficient temperature ranges for the experiments of this chapter is appended.

VAPOR PRESSURES OF SODIUM AND MERCURY[1]

Mercury		Sodium	
T, °C.	p, mm. Hg	T, °C.	p, mm. Hg
0	1.85×10^{-4}	0	6.3×10^{-13}
20	1.20×10^{-3}	50	7.1×10^{-10}
40	6.08×10^{-3}	100	1.2×10^{-7}
60	2.52×10^{-2}	150	6.3×10^{-6}
80	8.88×10^{-2}	200	1.4×10^{-4}
100	2.73×10^{-1}	250	1.7×10^{-3}
120	7.46×10^{-1}	300	1.37×10^{-2}
140	1.84	350	9.80×10^{-2}
160	4.19	400	3.44×10^{-1}
180	8.80	450	1.23
200	17.29	500	3.75
220	32.13	550	9.95
240	56.86	600	23.6

8-4. Quenching of Resonance Radiation.—It has been found that the intensity of the resonance radiation may be reduced by the introduction of a foreign gas into the resonance tube. Thus Stuart[2] found that hydrogen at a pressure of 1.2 mm. Hg reduced the intensity of the 2536 line reemitted by the mercury vapor to about 12 per cent of its intensity when no hydrogen was present. The mercury vapor after absorbing the incident light (2,536.52 Å = 39,412.6 wave numbers) is in the state $6s6p\ ^3P_1$ and hence contains an excitation energy of 39,412.6/8106 = 4.86 electron volts. The energy required to dissociate a hydrogen molecule into two atoms is known to be only 4.34 electron volts. If a collision occurs between an excited mercury atom and a hydrogen molecule during the 10^{-7} sec. that the former exists, an opportunity is presented for the excitation energy of the mercury atom to cause dissociation of the hydrogen resulting in two hydrogen atoms and a mercury atom in its normal state, $6s^2\ ^1S_0$, without the production of any radiation. The excess energy, $4.86 - 4.34 = 0.52$ electron volt, presumably appears as kinetic energy of the hydrogen and mercury atoms involved. Such a collision in which an excited atom gives up its excitation energy without the production of radiation is known as a *collision of the second kind.* A *collision of the first kind* is said to occur when the kinetic energy of an electron, for instance, is transferred to a normal atom at an impact resulting in its elevation to an excited state.

Often the quenching effect of a foreign gas is due not to the dissociation of a molecule but to the excitation of the foreign atoms or molecules present. Nor is it necessary that the originally excited atom return to its normal state, as in the example of the previous paragraph; it may be transferred to some metastable level from which the transition to the normal state is forbidden by a selection rule. The atom then remains in the metastable state until it is raised to an ordinary excited state by the absorption of a suitable quantum of radiation, or until a collision with another atom or the walls of the vessel allows this excitation to be transformed into kinetic energy. This situation arises in a mixture of mercury atoms and nitrogen molecules. If a mercury atom in the $^3P_1$ state collides with a normal nitrogen molecule, the former can be transferred to the lower metastable $^3P_0$ level by giving up 0.218 electron volt of excitation energy of which 0.19 volt is absorbed by the nitrogen molecule in a transition between two of its vibrational energy states, the remainder presumably appearing as kinetic energy of the particles. It is also possible for a reverse exchange of energy to occur; mercury in the $^3P_1$ state can be raised to the $^3P_2$ level by receiving kinetic energy from a fast nitrogen molecule to the extent of 0.57 electron volt. Both these transitions, by depopulating the $^3P_1$ state, reduce the intensity of the 2536 resonance radiation which is due to the jump from $^3P_1$ to $^1S_0$.

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[1] "International Critical Tables," vol. 3, pp. 205–206, McGraw-Hill 1928).

[2] STUART, *Zeits. Physik*, **32**, 262 (1925).

Definite evidence of such energy transfers was obtained by Wood,[1] in 1924, who illuminated a quartz tube, containing mercury and a few millimeters pressure of nitrogen, by the radiation from a quartz mercury arc lying parallel to the tube. A second mercury arc sent light lengthwise through the mercury and nitrogen mixture, and it was observed that the 4046 Å line from this arc was greatly reduced in intensity after passage through the resonance chamber. In emission, this line is due to a transfer from $6s7s\ ^3S_1$ to $6s6p\ ^3P_0$; the reverse process of absorption can therefore occur only if there is a large population of atoms in the $^3P_0$ state, which condition is brought about by collisions of the second type between nitrogen molecules and excited mercury atoms in the $^3P_1$ level, these having been produced by absorption of the 2536 line from the primary arc.

It has been found that the probability of the interchange of excitation energy between two systems at a collision, as described above, increases as the amount of excess energy to be dissipated in the kinetic form decreases; *i.e.*, the more exactly the two excitation energies coincide the more likely the process is to occur. It should be noticed that it is impossible for a mercury atom to change from any level of a ^3P multiplet to any other level in the same multiplet by the usual means of absorbing or emitting radiation; intramultiplet transitions are forbidden by the L selection rule. It is, of course, possible that second-type collisions between two mercury atoms, say in the $^3P_1$ and $^3P_0$ states, will result in the interchange of their energy without radiation, but as the atoms are indistinguishable the change cannot be detected and in effect accomplishes nothing.

[1] WOOD, *Proc. Roy. Soc.*, **106**, 679 (1924); *Phil. Mag.*, **50**, 774 (1925).

8-5. Experiments on Sensitized Fluorescence.—We have seen that excitation energy may be transferred from one system to another in a process known as a second-type collision. The example given of mercury in the $^3P_1$ state being reduced to the $^3P_0$ state by exciting a nitrogen molecule raises the question as to what happens to this energy acquired by the nitrogen. The amount transferred is 0.19 electron volt, so that, if the nitrogen returned to its original state by emitting radiation, this would have a wave length such that it would be in the extreme infra-red.

$$(0.19 \times 8{,}106 = 1{,}540 \text{ cm.}^{-1} = 64{,}935 \text{ Å})$$

Examples can be found, however, where radiation of a convenient wave length is produced by a second-type collision between two types of atoms, one of which was originally excited by light of a different wave length. The resulting emitted light is known as *sensitized fluorescence.*

Cario and Franck[1] placed some mercury and thallium in a quartz tube, an appreciable fraction of the atoms being kept in the vapor state by heating the whole apparatus in an oven to 800°C. Light from a quartz mercury arc fell on this tube, the line 2536 was absorbed and certain thallium lines were observed to be reemitted. The process may be described as follows. An excited mercury atom possesses 4.86 electron volts of energy, and at a collision of the second type with a normal thallium atom a fraction of the energy, equal to 4.46 volts, may be transferred resulting in excitation of the latter from the $^2P_{\frac{1}{2}}$ state to the $^2D_{\frac{3}{2}}$ state, the previously excited mercury atom returning to its normal state without the emission of radiation. The energy remaining after the exchange, 0.4 electron volt, appears as kinetic energy divided approximately equally between the two atoms as a result of the conservation of momentum since the two particles differ very little in mass. The excited thallium atom then returns to the normal state, $^2P_{\frac{1}{2}}$, emitting the line at 2768 Å, or to the excited level $^2P_{\frac{3}{2}}$ with the emission of the line at 3529 Å. It is also possible that a smaller energy transfer may take place at the second-type collision resulting in the excitation of the thallium atom to the $^2S_{\frac{1}{2}}$ state, requiring only 3.27 electron volts. As before, the mercury atom returns to its lowest level without radiating, and the two particles fly apart with still greater speeds due to the large excess energy of 1.59 volts. The return of the thallium to the low $^2P_{\frac{1}{2}}$ or $^2P_{\frac{3}{2}}$ states results in the emission of the line at 3776 Å or the line at 5350 Å.

Positive evidence that the excess energy is dissipated as kinetic energy is supplied by the comparative intensities of the reradiated thallium lines 2768 and 3776. The former is due to a transition which starts from a rather slowly moving atom in the $^2D_{\frac{3}{2}}$ state; the latter is emitted, according to the hypothesis, from a rapidly moving atom which is in a $^2S_{\frac{1}{2}}$ state before emission. Both jumps terminate in the normal state, so that the lines are capable of being reabsorbed by normal thallium atoms before the light leaves the tube. The reradiated light at approximately 3776 Å may be expected to have its frequency altered appreciably because of the Doppler effect produced by the rapid motion of the emitting atom; hence the resonance for absorption is not so close, and most of the light should make good its escape from the tube. On the other hand, the frequency of the light at 2768 Å is scarcely changed by the slowly moving atom that emits it, and its chance of escaping without being reabsorbed is much less. Actually the intensity of 2768 is found to be much less than that of 3776, which tends to confirm the supposed mechanism.

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[1] Cario and Franck, *Zeits. Physik*, **17**, 202 (1923).

It is of interest to notice that Cario and Franck observed thallium lines reradiated that were due to transitions from states further above the normal level than the 4.86 volts that could be supplied by an excited mercury atom. A series of auxiliary experiments showed that the line at 2536 Å, and only this line, was necessary in the exciting lamp, and that, furthermore, the anomalous thallium lines appeared only when the furnace was at the high temperature of 800°C. Evidence is thus furnished that the excitation energy of the mercury and the kinetic energy of thermal motion may combine in one elementary act to raise a thallium atom to a high excited state.

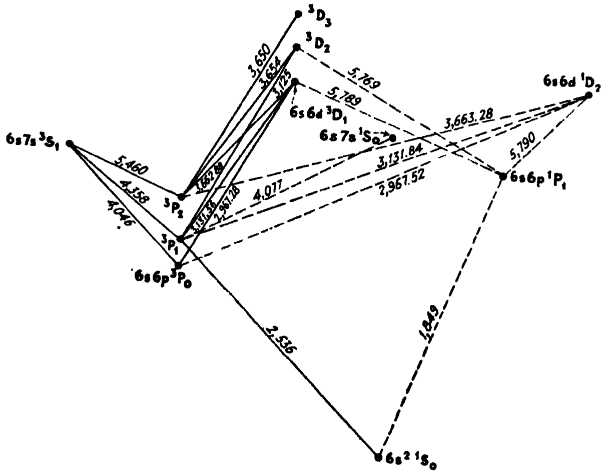

FIG. 8-3.—The Grotrian diagram of transitions in mercury involving the ^3P multiplet. Full lines indicate the wave lengths observed in sensitized fluorescence; dotted lines represent transitions that are not observed, for either theoretical or experimental reasons. Not to scale.

Sensitized fluorescence of light from the same type of atom as is initially excited can be demonstrated very beautifully with mercury vapor to which nitrogen has been added. As we have seen, mercury vapor irradiated with the 2536 line absorbs this color, the atoms being raised from the $^1S_0$ to the $^3P_1$ state. Collisions of the second kind with nitrogen molecules may result in the excited mercury atoms being transferred to the neighboring $^3P_0$ or $^3P_2$ levels, both of which are metastable, since there are no permitted radiative transitions by which they can be emptied. If the resonance tube is illuminated by all the radiation from a mercury arc, then during the relatively long lifetimes of the $^3P_0$ and $^3P_2$ states, there is a good chance that atoms so excited will be struck by quanta of the wave lengths 4046 Å and 5460 Å, absorption of which transfers the atoms to the higher $6s7s\ ^3S_1$ level. The metastable states thus act as quasi-normal or ground levels from which absorption is quite probable. Having reached the $^3S_1$ level, the atom may then return to the ^3P multiplet by emission of any of the 5460 Å, 4358 Å, or 4046 Å lines. In a similar manner, absorption of the proper wave lengths can carry the atoms from the metastable $^3P_0$ and $^3P_2$ states to the three levels of the ^3D multiplet, return from these being accomplished by the emission of six lines in the ultra-violet. These processes are represented schematically in the partial Grotrian diagram of mercury shown in Fig. 8-3. The full lines indicate the colors which are observed in sensitized fluorescence, the dotted lines represent transitions that are not observed for either theoretical or experimental reasons. The fact that the line at 4077 ($6s6p\ ^3P_1 - 6s7s\ ^1S_0$) is not observed, indicates that no absorption takes place from the unstable $^3P_1$ level. This consideration rules out any absorption of 3131.84 ($6s6p\ ^3P_1 - 6s6d\ ^1D_2$) which lies so close to 3131.56 ($^3P_1 - {}^3D_1$) that it cannot be resolved with a small instrument. Absorption of 3663.28 and 2967.52 would lift the atom from the $^3P_2$ and $^3P_0$ states up to the $6s6d\ ^1D_2$ level, and the reemission of these lines might not be detected due to their close proximity to the observed lines 3662.88 and 2967.28; these transitions do not occur, however, for the $^1D_2$ could also be emptied by the radiation of 5790 during a jump to $6s6p\ ^1P_1$, and this line is not observed. The lines 5769 and 5789, due to transitions from $^3D_2$ and $^3D_1$ to $^1P_1$, do not occur with sufficient intensity to be observed. It is conceivable that the higher members of the sharp series should also be absorbed and reemitted ($6s6p\ ^3P - 6s\,ns\ ^3S_1$), but these lines are comparatively faint in the exciting arc and hence might be expected to escape detection in the resonance observation. Similar considerations apply to the higher members of the diffuse

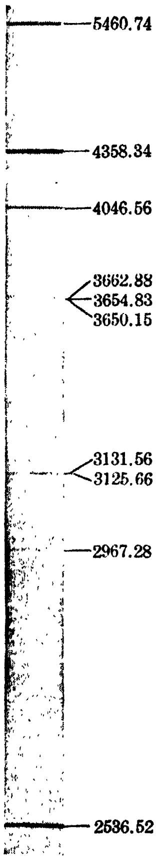

Fig. 8-4.—The sensitized fluorescence spectrum of mercury, obtained by irradiating a mixture of mercury vapor and nitrogen with the light from a quartz mercury arc.

series ($6s6p\,^3P - 6s\,nd\,^3D$). Figure 8-4 represents a picture taken with the resonance tube to be described presently, using a small quartz spectrograph, panchromatic plate, and an exposure of about 5 min. Only the 10 lines of the mercury spectrum indicated in Fig. 8-3 are seen to be present.

It is obvious that this experiment contains within it the simple phenomenon of resonance radiation, for the 2536 line is emitted with great intensity along with the others. The presence of nitrogen at 4 or 5 mm. Hg quenches the resonance radiation to about 80 per cent of its nitrogen-free value; *i.e.*, about 20 per cent of the mercury atoms in the $^3P_1$ state suffer second-type collisions with nitrogen molecules. The absorption of the line 2536 is a necessary antecedent to the production of the nine other colors in fluorescence. If a piece of glass, which is opaque to 2536, is interposed between the light source and the resonance tube, both of which are of quartz, all fluorescence completely ceases. If a fresh dilute solution of quinine sulphate in a quartz cell, such as a length of quartz tube stopped at both ends with corks, is interposed, a large fraction of the 4046 line from the arc is removed. As this is necessary to elevate an atom from the $^3P_0$ to the $^3S_1$ state and as the $^3P_0$ is much more densely populated than the $^3P_2$ level, a marked reduction of intensity of the $^3P - {}^3S$ multiplet, in comparison with the 2536 line, is observed. Further evidence that the assumed explanation is correct is furnished by the use of a screen, such as a piece of fine copper gauze which transmits, say, $1/q$th of the light falling on it. If such a screen is introduced between the resonance lamp and the spectrograph, the observed intensity of each of the emitted lines falls to $1/q$th of its former value. If the screen is placed between the light source and the resonance chamber, the intensity of each of the reemitted lines (except 2536) is cut to $1/q^2$ of the value with no screen, for the lines are excited in two steps by two colors of the incident light both of which are reduced by a factor $1/q$. Intensity measurements on a photographic plate are rather uncertain without the use of a densitometer, but the above prediction can be shown to hold to within 2 or 3 per cent by the use of an ordinary photoelectric cell connected to a battery and galvanometer of high current sensitivity in place of the spectrograph. Light from the resonance tube is focused by means of a lens on to an opening in a black-paper shield surrounding the photoelectric cell. This arrangement records the integrated intensity of all the lines; the glass bulb of the cell and the lens, if a glass one is used, conveniently cut out the reemitted 2536 line. Some of the lines of the ^3D multiplet are also not recorded depending on the thickness of the glass, but the above relation will hold for whatever lines do penetrate to the active surface of the cell. It is not necessary to measure q directly. If the galvanometer deflections are d_1 when no screen is used, d_2 when it is placed before the photoelectric cell, and d_3

when between the light source and the resonance tube, we should find the relation

$$\left(\frac{d_2}{d_1}\right)^2 = \frac{d_3}{d_1}$$

A resonance tube which has been used successfully in the above experiment is of fused quartz about 1 in. in diameter and 6 in. long. A plane quartz window is fused into one end and the other terminates in an absorbing horn. A graded quartz-to-glass side tube, with a constriction in the quartz portion for sealing off, permits attachment to the pumping system. The tube is baked in an electric furnace for several hours at 500°C. while being evacuated in order to thoroughly out-gas the walls. A small quantity of mercury is then distilled over from an appendix, and nitrogen is admitted from an auxiliary system until the green fluorescence caused by a quartz mercury arc in close proximity is quite intense; the pressure is not critical over a range of roughly from 2 to 8 mm. Hg. The tube is then carefully sealed off the vacuum system.

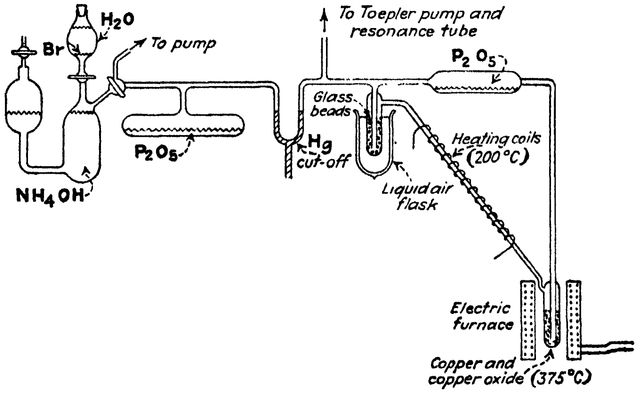

FIG. 8-5.—A generating and purifying system for nitrogen.

The nitrogen must be of great purity. It may be prepared by dropping bromine into ammonium hydroxide, several liters of the gas being made and pumped off to flush out the chamber. The final supply is stored over phosphorus pentoxide for several days to remove water vapor. This gas is then admitted, at a pressure of about 10 cm. Hg, to a system where it is circulated through copper filings and copper oxide maintained at 300° or 400°C., a liquid air trap, and phosphorus pentoxide. The hot copper and copper oxide remove oxygen and hydrogen with the production of water; this is removed by the liquid air and phosphorus pentoxide, the former also removing any other condensable vapors. Circulation is maintained by passing a current through a heating coil surrounding the tube leading upward from the copper to the liquid-air trap; the cold gas then descends through the drying chamber to the copper again. This circulation is maintained for about 24 hr., and the nitrogen is then sent to the resonance tube by means of a Toepler pump. The experimental arrangement is indicated in Fig. 8-5.

To obtain intense fluorescence of the mercury vapor, it is advantageous to illuminate the tube from the side by a parallel mercury lamp and to observe lengthwise through the end window toward the blackened background formed by the horn. For this purpose the resonance lamp should be painted a dull black except over the end window and a long opening down one side. A convenient and very intense mercury lamp can be made from a quartz tube $\frac{1}{2}$ in. in diameter and 3 or 4 in. long. To one end of this tube is fused, by means of a graded seal, a glass tip containing an 80-mil tungsten rod terminating in a cylindrical nickel electrode to facilitate the dissipation of heat. The other end is similarly joined to a glass bulb which houses a large heater-type filament. The latter is a heavy tungsten coil surrounded by a nickel cylinder about 1 in. long and $\frac{3}{8}$ in. in diameter. This should be painted with a mixture of barium and strontium oxides suspended in varnish in order to secure a copious electron emission. These sources may be constructed quite simply, or they may be obtained commercially. The apparatus is then connected through a side tube to an evacuating system, a few drops of mercury are introduced, and the arc is run for several hours for thorough out-gassing of the electrodes before sealing off. The filament current of 6 or 8 amp. may be supplied by a step-down transformer; the arc itself runs on about 50 or 60 volts, the current consumption from the 110-volt direct-current mains being limited by a series rheostat to about 1 amp. To start the lamp it is generally necessary to approach it with some source of alternating high potential such as a vacuum leak tester or one terminal of a small induction coil. If desired, an electromagnet may be mounted so as to force the discharge to the wall nearest the resonance tube and thus decrease the self-reversal of the 2536 line, but this procedure is not essential.

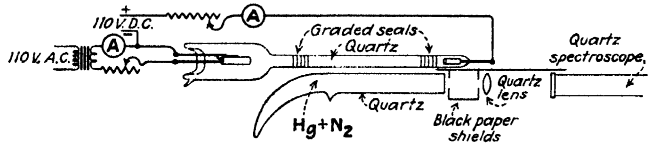

FIG. 8-6.—A quartz resonance tube and mercury lamp for observing sensitized fluorescence in a mixture of nitrogen and mercury vapor.

8-6. Experiments on the Raman Effect.—We have found evidence that an atomic system is capable of absorbing completely a photon with which it collides, provided the energy of the photon is exactly the requisite amount to transfer the atom to an excited state, and provided, furthermore, that the consequent changes in the quantum numbers are permitted by the selection rules governing the emission of radiation. When thus absorbed the photon loses its identity as an indivisible packet of energy, for we have seen that the resultant excitation energy of the atom can be disposed of in sections, part being transferred into excitation of another atom or molecule and part appearing as kinetic energy of the collision partners. This suggests the possibility of a still different method of energy interchange between radiation and an atomic system. The collision of a photon with an atom or molecule may result in the absorption of part of the energy of the photon. Or, more generally still, the photon may either gain or lose energy at a collision, the energy transferred being equal to the difference between two stationary states of the system with which it collides. The possibility of such an occurrence was first predicted by Smekal[1] in 1923 and was confirmed experimentally 5 years later by Raman[2] for the case of liquids, and almost simultaneously by Landsberg and Mandelstam[3] for solids.

The theoretical considerations are extremely simple. Suppose a photon of energy $h\nu$ and momentum $h\nu/c$ collides with a molecule having a kinetic energy $mv^2/2$ and an internal energy of excitation E_a. Let us assume that as a result of this collision a photon is emitted with energy $h\nu'$ and momentum $h\nu'/c$ while the molecule is left with a kinetic energy $mv'^2/2$ and an internal energy E_b. From the conservation of energy we have

$$h\nu + \frac{mv^2}{2} + E_a = h\nu' + \frac{mv'^2}{2} + E_b$$

The kinetic theory of gases shows that in a swarm of two kinds of particles of masses M_1 and M_2, where $M_1 > M_2$, the average fraction of the kinetic energy gained by the heavier particle at a random collision is of the order of $2M_2/M_1$. Considering that a photon has a mass of $h\nu/c^2$, of the order of 10^{-33} gram for visible light, and that a molecule has a mass of the order of 10^{-23} gram, only a fraction equal to about 10^{-10} of the kinetic energy of the light particle is transferred to the molecule at a collision. This is a completely negligible quantity and we may take v as equal to v' in the above expression, giving

$$\nu - \nu' = \frac{1}{h}(E_b - E_a)$$

or

$$\Delta\nu = \nu_{ab}$$

where ν_{ab} represents the frequency associated with the energy transition in the molecule. The photon may thus be expected to recoil with a higher or lower frequency corresponding to a quantized decrease or increase in the molecular excitation energy. The situation where E_a and E_b are equal corresponds to an elastic collision, no energy being exchanged between the photon and molecule. When the frequency of the light is decreased by the collision, the resultant spectral line is known as a *Stokes line*, by analogy with the typical Stokes fluorescence wherein the emitted light is of longer wave length than the exciting radiation. Correspondingly, a photon which gains energy at a collision is said to give rise to an *anti-Stokes line.*

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[1] Smekal, *Naturwiss.*, **11**, 873 (1923).

[2] Raman, *Indian J. Phys.*, **2**, 387 (1928).

[3] Landsberg and Mandelstam, *Naturwiss.*, **16**, 557, 772 (1928).

As most of the permissible energy changes in atomic systems involve radiations of visible or ultra-violet wave lengths, ν_{ab} is so large that a photon of visible light suffering an inelastic collision of this type with an atom would be scattered with a new frequency far in the extreme infra-red or ultra-violet where observational difficulties are very great. On the other hand, molecular energy levels are so close together that radiation due to transitions between them lies in general in the far infra-red. Hence ν_{ab} is quite small, relatively speaking, and visible light scattered from molecules should show a change in wave length of only a few Ångströms.

The accompanying photographs show the results of observing with a small glass spectrograph the light scattered by carbon tetrachloride and water, when irradiated with light from an ordinary glass mercury arc. In spite of the relatively long exposures, the mercury lines are not greatly overexposed, indicating that these lines are not due to direct reflection from the walls of the vessel but to elastic collisions with the molecules of the scattering substance. In the case of carbon tetrachloride, five Stokes lines can be seen on the long wave-length side of the mercury line 4358 and three anti-Stokes lines toward the violet, the latter being of considerably less intensity. Similar groups appear near the less intense exciting lines 5790, 5460, and 4046. Wave-length measurement of the plate gives values for these Raman lines which permit them to be classed as due to these four mercury lines, for on this basis each group shows the same wave-number separation from the chosen parent line. The separations, as found with a spectrograph of high dispersion, are 217, 313, 459, 760, and 791 wave numbers; an additional faint line at 1,537 is not seen in this photograph. Measurement with a small instrument gives values agreeing to within two or three units with the above values. In the case of water the Raman lines are very diffuse, but the unresolved band corresponds to a wave-number change of about 3,420. On our theory this should be confirmed by the presence of an absorption band at about 2.9μ ($\mu = 10^{-4}$ cm.); reference to the black-body distribution curves in Chap. II shows that an absorption band in ordinary humid air is actually observed at that wave length. (This, however, is not conclusive evidence, as a carbon dioxide absorption band occurs in the same neighborhood.)

If the theory is correct the carbon tetrachloride lines should also correspond to the wave numbers of possible infra-red radiations of wave lengths 46.09, 31.95, 21.78, 13.16, 12.64, and 6.51 μ units. Experiments on the infra-red absorption spectrum of carbon tetrachloride[1] show absorption bands at 13.10, 12.72, and 6.45 μ in quite good agreement with the Raman lines; measurements beyond 15μ have not been made. There are, however, certain peculiarities; these infra-red bands are very strong, while the corresponding Raman lines are extremely faint; also a number of other absorption lines are not represented by any Raman lines at all. Hence, although Smekal's simple interpretation of the Raman effect appears to be correct in general, some further restriction is necessary to account for the intensities. This has been given by Langer[2] and Rasetti,[3] who have shown on quantum mechanical grounds that the intensity of a Raman line, due to a transition between levels E_a and E_b, increases with the number of other terms with which both E_a and E_b combine. Thus for a Raman line to occur at all, due to the change from E_a to E_b, there must be at least two normal emission lines given by jumps from E_a and E_b to a third level E_c; if a fourth level E_d combines in emission with both E_a and E_b, the Raman line $E_a - E_b$ will be more intense. The Raman lines are in general due to transitions which would ordinarily be forbidden by the selection rules; the displaced lines can therefore afford information about molecular energy levels which would otherwise be unobtainable. On this basis, Langer has postulated a system of energy

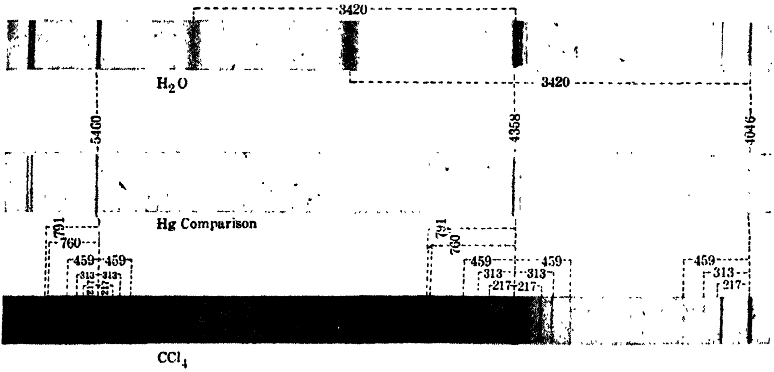

FIG. 8-7.—The Raman spectra obtained from water and carbon tetrachloride when irradiated with the light from a mercury arc. An ordinary mercury spectrum is included for comparison.

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[1] LE COMPTE, "Le Spectre Infrarouge," p. 213, Presses Universitaires de France (1928).

[2] LANGER, *Nature*, **123**, 345 (1929).

[3] RASETTI, *Proc. Nat. Acad. Sci.*, **15**, 234 (1929).

levels for carbon tetrachloride, so chosen as to represent correctly the observed Raman lines; an excellent check is obtained on comparing the predicted infra-red wave lengths with those found experimentally. An extensive treatment of the experimental and theoretical aspects of the Raman effect has been given recently by Kohlrausch.[1]

The Raman effect in liquids is quite simple to observe using a technique developed by Wood.[2] The liquid to be investigated is placed in a glass tube, closed at one end with a plane window and terminated at the other with a blackened horn, as in the experiments on resonance radiation. For the most efficient operation this tube should be at least as long as the effective region of the exciting arc. It is mounted immediately below and parallel to an intense helium or mercury arc. A semicylindrical polished tin or aluminum reflector is bent around the lower half of the Raman tube and a similar but larger reflector hung over the exciting arc. Filters for isolating certain of the strong lines may be interposed between the arc and the scattering vessel if desired. This is always to be recommended, particularly if the Raman separations are at all large, as otherwise the determination of the proper parent for weak Raman lines is likely to be uncertain. A short-focus lens immediately in front of the plane window at the end of the tube directs the scattered radiation upon the slit of a spectrograph which is carefully aligned along the tube's axis and screened from the direct radiation of the arc. Alternatively, a system of diaphragms and a lens, as indicated in Fig. 8-6, may be used. The stronger Raman lines of a liquid such as carbon tetrachloride may be photographed in less than an hour with a small spectrograph, but the complete set may require up to ten or fifteen hours, depending largely on the brilliance of the arc, the speed of the spectrograph, and the intrinsic intensity of the Raman lines. The quartz or glass mercury arcs or the glass helium arcs of the General Electric Vapor Lamp Company are very convenient sources.

It is necessary, when using arcs which become very hot, to surround the Raman tube with a water-cooling jacket to prevent the liquid from boiling. This may be a glass tube of somewhat larger diameter than the Raman chamber and slightly shorter than its straight portion. The two tubes are mounted coaxially and held in place with two large rubber corks through which holes have been cut for the scattering tube. To cut a smooth hole in a rubber stopper it is convenient to force it into the end of a metal tube of suitable diameter mounted in the chuck of a lathe. A penknife moistened with a solution of sodium hydroxide or glycerin is pressed normally against the spinning rubber which under this treatment cuts very easily. Entrance and exit tubes for the circulating water are sealed into the jacketing chamber near the ends. This surrounding jacket may also be used as the light filter by dissolving the appropriate substances in the circulating water.

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[1] Kohlrausch, "Der Smekal-Raman Effekt," Springer (1931).

[2] Wood, *Phil. Mag.*, **6**, 729 (1928); *Phys. Rev.*, **37**, 1022 (1931).

Certain convenient filters for isolating lines from mercury or helium arcs are given in the following table; a more extensive list is to be found in the literature to which reference has been made.

Helium	Mercury	Filter
5875	5791 5769	Corning No. 348 (and No. 430, if elimination of the red is desired), or Wratten No. 22, or Chrysoidin and eosin, or concentrated potassium bichromate solution
	5461	Corning No. 351 and No. 512 (5 mm.) (trace of yellow), or Wratten No. 62 or No. 77, or No. 77-*A* (last two most satisfactory), or Dilute potassium bichromate and neodymium nitrate solution
4471	4358	Corning No. 038 and No. 511 (3 mm.), or Wratten No. 50 (blue and violet lines) Shorter wave lengths may be cut out by Corning Noviol which removes the 3650 lines and protects a subsequent layer of 0.3 per cent quinine sulphate solution acidulated with sulphuric acid to remove the 4046 line, or 12 mm. of a saturated solution of sodium nitrite may be used in a container of ordinary glass
	4077 4046	Corning No. 306 (2 mm.), and No. 597 (6 mm.), and No. 428 (4 mm.), or Corning Noviol and iodine solution made by diluting a saturated solution 1:15 with carbon tetrachloride, or Corning Noviol and a solution of fluorescein
3888	3650	Corning No. 586 (8 or 9 mm. for the mercury lines) Corning No. 584 (2 or 3 mm. for the helium line)

8-7. Photo-ionization.—A further possibility for the interaction between a photon and a gas atom is that in which the photon has sufficient energy completely to remove an electron from the atom, the photon disappearing and a positive ion and free electron being the result of the encounter, any excess energy that remains after the collision appearing in kinetic form. This is obviously similar in some respects to the photoelectric effect from surfaces discussed in Chap. V, but there are important differences. In the surface effect the critical frequency, for less than which no electron emission occurs, is determined by the work function of the surface, there being as yet no theoretical way of predicting its value. For photo-ionization of gases, however, the complicating influences of crystal potential barriers are absent, since we are dealing with isolated atoms; the energy required to ionize a normal atom should be exactly equal to the energy of the normal state measured from the ion, as determined from spectral series. The critical wave length should therefore be equal to the series limit of the term series to which the lowest or normal state belongs. (This threshold energy in general is considerably greater than that of the surface photoelectric effect.) Since the dislodged electron can have any subsequent kinetic energy, ionization by all wave lengths less than the critical value should be possible, with the complete absorption of the photon, although it might be expected that the maximum probability should occur when the photon has just enough energy. Furthermore, if the conception is correct, the number of photoelectrons ejected from the gas should equal the number of photons that disappear in it.

Experimental work on photo-ionization in gases is beset with many difficulties, and only recently have reliable results been obtained. Primarily, the theoretical threshold wave lengths for almost all substances other than the alkalies are located so far in the ultra-violet that even fluorite is useless as a window; but for the alkalies the critical values lie between 3184 Å for caesium and 2300 Å for lithium, which is a convenient range for quartz containers and instruments. Consequently most of the work has been done with these elements. Intense ionization requires a large density of atoms, which is obtained by keeping the experimental tube quite hot; this causes the alkalies to attack the quartz windows and also to form highly sensitive photoelectric deposits on all the electrodes. Any scattered light falling on these surfaces causes the emission of currents much greater than those it is desired to measure.

Two general methods of measuring the formation of positive ions have been used. In one, an absolute determination of the ion current is made, by sweeping to an electrode with an electric field any ions formed in a jet of the material which issues from a furnace and which subsequently is frozen on a surface cooled by liquid air; the light beam is carefully prevented from falling on this sensitive deposit. In the other, no attempt at absolute measurement is made, but an amplifying device is used that avoids the difficulties of large photoelectric currents from the deposited films. This is the space-charge annulment scheme, originated independently by Kingdon[1] and by Hertz.[2] The vapor to be studied is enclosed inside a metal gauze cage in an evacuated vessel with a quartz window; a very hot fine tungsten filament inside the cage emits thermionic electrons which are drawn to the gauze by a rather weak field (less than

[1] KINGDON, *Phys. Rev.*, **21**, 408 (1923).

[2] HERTZ, *Zeits. Physik*, **18**, 307 (1923).

the ionizing potential of the vapor), so that a space-charge cloud of electrons is formed around the filament retarding the emission. If a positive ion is released in the body of the gas by the action of a photon, it is attracted to the filament and generally spirals around it many times before touching it; its continued presence therefore neutralizes a large number of electrons in the cloud, and a great increase in the thermionic electron current is observed. (Details of the circuit will be considered in a later section.) This method is not only exceedingly sensitive (although the amplifying factor is not constant), but it eliminates the effects of surface photoelectricity from the vapor condensed on the walls; any electrons emitted there are immediately drawn back by the electric field. The photoelectrons liberated from the small surface of the filament are entirely negligible.

The light source in the early work was usually a quartz mercury arc and a set of liquid or solid filters; much more reliable results have been obtained recently by the use of a quartz monochromator and either a quartz mercury arc or the continuous radiation from a quartz incandescent lamp, or from a powerful hydrogen discharge in a quartz capillary tube.

The recent work of Mohler,[1] Lawrence,[2] Freudenberg,[3] and others bear out, in the main, the predictions outlined above. For caesium and rubidium the ionization is a maximum at the wave length corresponding to the series limit and falls away at shorter wave lengths approximately proportionally to λ^3, indicating that the likelihood of ionization is greater when the excess energy to be turned into kinetic energy of the electron is small. Furthermore, in this wave-length region short of the threshold value, the number of ions formed seems to be qualitatively equal to the number of photons disappearing, within the rather wide limits of error, the photon absorption being determined by densitometer records of spectrograms taken of the radiation that has traversed the vapor. For potassium, the results are not so well in accord with prediction. Two ionization maxima have been found, one, rather weak, at the series limit and a much stronger one at a considerably shorter wave length. This was tentatively assigned to a potassium molecule, but further work indicates that molecules are only about $\frac{1}{100}$ as prevalent as atoms in such a vapor, so that the explanation does not seem adequate. There are some indications of a similar second ionization maximum for caesium.

Contrary to the expectations of simple theory, however, the ionization does not remain zero as the exciting light is reduced from long wave lengths until the series limit is reached; for rubidium and caesium appreciable ionization occurs at wave lengths corresponding to each member of the principal line series. Absorption of these lines represents transitions from the normal state ^2S to the excited ^2P levels; for none of these jumps is the energy great enough to cause ionization and yet it is observed. A variety of suppositions have been made to explain this anomaly, but the only one which has proved acceptable is that proposed by Franck: the collision of an excited atom with a neutral atom produces an ionized molecule whose ionization potential is sufficiently lower than that of the atom to allow ionization to take place with the small energy available. A similar phenomenon is observed with mercury. Spectroscopic data place the lowest term $6s^2\ ^1S_0$ at 84,178.5 wave numbers from the ion, corresponding to a threshold wave length of 1188 Å, and yet ionization is produced by irradiation with the 2536 Å line, although this should merely put the atom in the excited $6s6p\ ^3P_1$ state. Various arguments and further experimental investigations[1] indicate that the ionization is very probably caused in several steps: some of the atoms in the $^3P_1$ state are transferred to the lower and metastable $^3P_0$ level by collisions with normal mercury atoms, in which condition they have 4.64 electron volts of energy above the normal; here they remain for a comparatively long time until they collide with an atom in the $^3P_1$ state with 4.86 volts of energy. The sum, $4.64 + 4.86 = 9.5$, if taken up entirely by one atom, is still insufficient to ionize it, but there is reason to believe that a mercury molecule might have an ionization potential of less than this amount.

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[1] Foote and Mohler, *Phys. Rev.*, **26**, 195 (1925).
Mohler, Foote, and Chenault, *Phys. Rev.*, **27**, 37 (1926).
Mohler and Boeckner, *Bur. Standards J. Res.*, **3**, 303 (1929); **5**, 51 (1930).

[2] Lawrence, *Phil. Mag.*, **50**, 345 (1925).
Lawrence and Edlefsen, *Phys. Rev.*, **34**, 233, 1056 (1929).

[3] Freudenberg, *Zeits. Physik*, **67**, 417 (1931).

In addition to the possibility of observing ionization from the normal levels of the alkali vapors by means of ultra-violet light, a further method of attack lies in the critical absorption "edges" of the spectrum of X-rays that have passed through matter. As we shall see in Chap. IX, the absorption of X-rays is accomplished by the removal of an electron to the periphery of an atom from a low level; X-rays are then reemitted in random directions, as the electrons settle down to fill this inner vacated level. As the wave length of the incident X-rays is reduced, the photons acquire sufficient energy to ionize successively electrons lying in lower and lower states, with a corresponding absorption of the primary beam at each critical value. The probability of ionization is found to be greatest at these values, and the absorption falls off with λ^3 as the wave length is further reduced (Owen's law).

Thus we have evidence that whether an outer electron is removed (optical absorption) or an inner one (X-ray absorption), the probability of such ionization is zero until the incident photon has just the requisite amount of energy necessary for the process (excepting the cumulative action in the optical case); at this point it reaches a maximum and then falls rapidly away, more or less proportionally to λ^3 in general agreement with theoretical expectations. Complete discussions of photo-ionization and allied problems have been given by Franck and Jordan,[1] Pringsheim,[2] Mohler,[3] Hughes and DuBridge,[4] and Darrow.[5]

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[1] Houtermans, *Zeits. Physik*, **41**, 619 (1927).

8-8. The Compton Effect.—We have seen that the absorption of X-rays may occur as the result of ionizing one of the tightly bound inner electrons of an atom, the energy requirements and the probability of the occurrence being quite analogous to the ionization of an outer electron by ultra-violet light, the incident photon being completely absorbed in both cases. The ionization phenomenon analogous to the Stokes type of Raman excitation, wherein the photon loses only part of its energy, occurs when the ionizing energy of the electron is completely negligible compared to the energy of the photon that collides with it. In such a case, the neglect of the binding energy is equivalent to treating the electron as if it were actually free, and, as we have seen in Chap. VI, the photon then cannot completely disappear during the encounter. Either the remainder of the atom must share in the collision or a new photon must appear. Since we are now investigating the case when the atom's participation is vanishingly small, we must postulate the existence of an altered photon and must treat the problem as a three-body collision, wherein the conservation of momentum and of energy must be maintained. As a first approximation, we may assume that the electron is initially at rest.

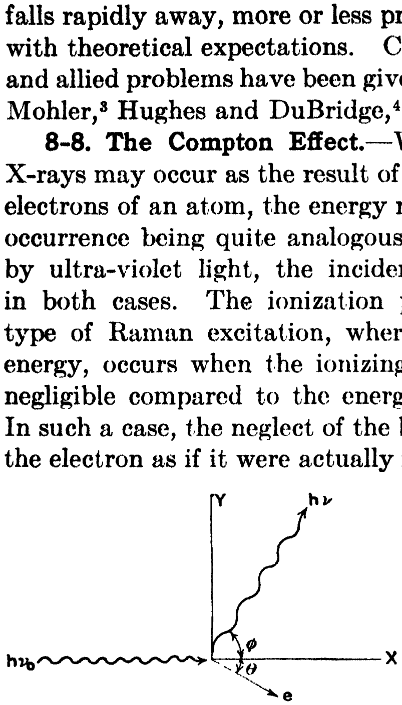

FIG. 8-8.—A diagram illustrating the Compton effect; the collision of a photon with a free electron initially at rest.

Thus, if a quantum of energy $h\nu_0$ which is moving along the X-axis is incident upon an electron, let us assume that a quantum of frequency ν travels off at an angle ϕ, and the electron recoils at an angle θ. As $h\nu_0/c$ and $h\nu/c$ are the momenta of the two photons, the equations for the conservation of momentum along the two axes are

$$\frac{h\nu_0}{c} = \frac{h\nu}{c}\cos\phi + m_0\beta v\cos\theta \tag{8-1}$$

$$0 = \frac{h\nu}{c}\sin\phi - m_0\beta v\sin\theta \tag{8-2}$$

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[1] FRANCK and JORDAN, "Anregung von Quantensprüngen durch Stösse," Springer (1926).

[2] PRINGSHEIM, "Fluorescenz und Phosphorescenz," Springer (1928).

[3] MOHLER, *Phys. Rev. Suppl.* (*Rev. Mod. Phys.*), **1**, 216 (1929).

[4] HUGHES and DUBRIDGE, "Photoelectric Phenomena," McGraw-Hill (1932).

[5] DARROW, *Bell System Technical J.*, **9**, 341 (1930); "Electrical Phenomena in Gases," Williams & Wilkins (1932).

where $\beta = \frac{1}{\left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}}}$, so that $m_0\beta v = mv =$ the momentum of the electron. Removing the terms containing θ to one side, squaring and eliminating this angle, we have

$$\left(\frac{h\nu_0}{m_0c^2}\right)^2 + \left(\frac{h\nu}{m_0c^2}\right)^2 - 2\frac{h^2\nu\nu_0}{m_0{}^2c^4}\cos\phi = \frac{v^2\beta^2}{c^2} \tag{8-3}$$

The equation for the conservation of energy may be written

$$m_0c^2 + h\nu_0 = m_0\beta c^2 + h\nu \tag{8-4}$$

As $(v\beta/c)^2 = \beta^2 - 1$, we may eliminate v and β from Eqs. (8-3) and (8-4) and obtain the following expression for the frequency ν of the resulting quantum

$$\nu = \frac{\nu_0}{1 + \frac{h\nu_0}{m_0c^2}(1 - \cos\phi)}$$

When $\phi = 0$ the incident and emerging quanta are seen to have the same frequency, but for all other angles of scattering the frequency of the emerging quantum is smaller. The loss of radiant energy which this represents is balanced by the kinetic energy of the recoiling electron. Thus this partial absorption of a quantum resulting in ionization causes a shift toward longer wave lengths of the emerging radiation; the exact value of the shift depending on the angle of scattering.

$$\Delta\lambda = \lambda - \lambda_0 = \frac{c}{\nu} - \frac{c}{\nu_0} = \frac{h}{m_0c}(1 - \cos\phi) \tag{8-5}$$

It will be observed that this change is independent of the original wave length. Putting in the values of h, m_0, and c, we obtain for the maximum shift, which occurs for $\phi = 180°$, the value 4.85×10^{-10} cm., and for the shift which would be expected at 90°, 2.42×10^{-10} cm. This wave-length change is very small, but it was detected by Compton[1] in 1922 using the K lines of the X-ray spectrum of molybdenum, scattered from a graphite block.

The experimental verification of this wave-length shift, obeying Eq. (8-5), gives very great support to the theory of collisions between photons and electrons which has been developed, and establishes the applicability of the laws of conservation of energy and momentum to these impacts. The fact that the electrons are not really free or initially at rest is evidenced by the breadth of the maximum representing the radiation scattered with a change in wave length. This maximum is considerably broader than that representing elastic photon scattering, but these are refinements which would take us beyond the field of our discussion.

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[1] Compton, A. H., *Bull. Nat. Res. Council*, No. 20, p. 16 (1922); *Phys. Rev.*, **21**, 715 (1923); **22**, 409 (1923).

8-9. Experiments on Excitation Potentials.—In the preceding sections we have investigated the ability of an atom to absorb energy in the form of radiation, and we have seen that the energy so absorbed is taken up selectively, the atom being raised from the normal to an excited state. Furthermore these radiative energy interchanges are observed to occur in such a way that the postulates made in regard to emission spectra, particularly with reference to the selection rules governing transitions accompanied by the emission or absorption of radiation, are entirely confirmed. In the present section we shall investigate the ability of an atom to absorb energy supplied in the form of the kinetic energy of a bombarding electron. On the basis of the previous sections we should anticipate that the kinetic energy of an electron is also absorbed selectively in amounts corresponding to the energies of the various stationary states above the normal level of the atom. However, the selection rules we have used in the past may lose their validity, as the mechanism, whatever it is, for the absorption of a photon may be entirely different from that for the absorption of the kinetic energy of an electron. If the values of the energy levels found with electron bombardment compare favorably with those deduced spectroscopically, we are afforded the most direct and convincing evidence that the stationary state concept is correct. Exact agreement cannot be expected, since an error of 0.1 volt corresponds to 810 wave numbers.

There are a number of experimental methods by which the problem may be attacked. We may focus our attention on the electrons and measure their residual energy after they have been accelerated by an electric field through a region containing atoms of the gas or vapor. If the atoms are capable of absorbing energy only in the characteristic amounts indicated by our previous theory, the collisions will be perfectly elastic (no energy will be lost by the electrons), until the electrons have progressed far enough through the field so that their energy is equal to, or slightly greater than, the lowest of these critical amounts. Then, at a collision, this kinetic energy may be lost to an atomic system raising it to the lowest excited state; as a first approximation the electrons will be brought to rest. If they are still in an electric field after the collision, they may gain more energy and repeat the process. If an inelastic collision does not occur as soon as an electron acquires sufficient energy, it may gain enough more to excite a higher state of the atom. Thus, as the potential difference between the electrodes is increased, the residual energy of the electrons should pass through maximum and minimum values, the maximum values occurring just before one of these characteristic energy losses. This residual energy of the electrons is measured by means of a retarding potential against which they must be able to travel in order to be recorded by a galvanometer. As an alternative method of observing these critical energy losses, the radiation emitted by the atoms which have been raised to excited states at inelastic collisions may be detected by either photoelectric or spectroscopic means. This technique, however, is more difficult. Finally, for the measurement of the series limit, *i.e.*, the energy necessary to remove completely an electron from an atom, we may investigate the particular electron speeds at which positive ions are formed in the gas.

The original so-called partial-current method of Franck and Hertz[1] is a simple and effective way of examining the changes in the residual electron energies as the total potential difference is varied through which the electrons fall in passing through a gas or vapor. It is suitable for inert gases and metallic vapors since these have no appreciable electron affinity, *i.e.*, there is no tendency for an electron to become attached to an atomic system, resulting in a negative ion. It is particularly appropriate for use with high pressures. In this method, electrons from a filament are accelerated by a variable potential V_a toward a grid, and, if they have lost no energy at the impacts occurring between these electrodes, they are capable of advancing further against a very small retarding field V_r between this grid and a collecting plate. The electrons reaching the plate are recorded by a galvanometer. As the accelerating potential V_a is increased from a small value, the electron current to the plate also rises. In this region, elastic collisions with the gas atoms occur and the original direction of motion of an electron is altered, but eventually almost all of the electrons reach the plate. When, however, V_a is equal to, or slightly greater than, the minimum excitation potential of the gas, some of the electrons collide inelastically, and the energy which they possess after exciting an atom is insufficient to allow them to proceed against the retarding field V_r, and the galvanometer current drops off. The current does not decrease abruptly, for, as the potential difference is increased, the inelastic collisions are able to occur nearer the filament and many of the electrons are able to gain sufficient energy after the collision to surmount the potential barrier V_r and to reach the collecting plate. Also, as we have seen, the electrons are emitted from the filament with a distribution of velocities which tends to smooth out any sharp discontinuities in the curve. As the potential difference is increased, the electrons gain sufficient energy again to excite the lowest level of another atom and a second decrease in galvanometer current is observed.

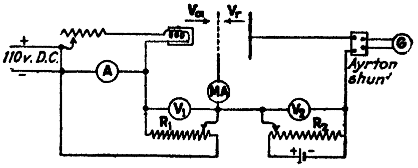

FIG. 8-9.—A diagrammatic sketch of the Franck and Hertz partial-current method of detecting inelastic impacts of electrons with gas atoms.

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[1] FRANCK and HERTZ, *Verh. Deut. Physik. Ges.*, **16**, 10 (1914).

We thus expect a series of maxima and minima in the galvanometer current, corresponding to single and multiple inelastic collisions, as the accelerating potential is increased. A high concentration of atoms in the space traversed by the electrons favors the occurrence of inelastic collisions at which the lower excited states are produced, for the free paths between collisions are shorter and there is a correspondingly smaller chance that an electron can gain sufficient energy between inelastic collisions to excite the higher states. The investigation of such higher levels is more feasible at small gas pressures and with a more refined type of apparatus.

Quite acceptable determinations of the lower energy levels of the mercury atom can be made with a General Electric thyratron. This is a vacuum tube containing a small amount of mercury; the small three-electrode type such as the FG-27 is suitable for this experiment. The density of the mercury vapor in the region surrounding the electrodes can be controlled by placing the tube in a small electric oven. Such an oven can be made conveniently of heavy asbestos board with about 10 ft. of nichrome heating wire in the form of a $\frac{1}{2}$-in. helix fastened around the inside of the walls. A mercury thermometer or calibrated thermocouple capable of covering the range from room temperature to about 250° C. may be used to measure the temperature. The electrical connections are shown in Fig. 8-9. If direct current is available, the same supply may be used for the filament and for the accelerating potential, as shown in the diagram. Otherwise a step-down transformer may be used for heating the filament and small-capacity dry cells for the accelerating potential V_a. This potential is controlled by the potentiometer R_1 and measured with the voltmeter V_1, which should be read to 0.1 volt. The milliammeter in the grid circuit is not essential. The small constant retarding potential V_r is supplied by the battery and potentiometer R_2. This potential, as measured by V_2, may be conveniently chosen at about 0.5 volt; the value is not critical. The galvanometer should be of moderate sensitivity; one giving a deflection of 2,000 mm. at a meter per microampere is adequate.

Figure 8-10 indicates typical results obtained with an FG-27 thyratron maintained at 210° C. The vapor pressure at this temperature is about 24 mm. Hg, and the density of the atoms is so great that only the lowest excited state is ever produced. The presence of a contact potential between the filament and grid vitiates the absolute readings of the voltmeter; however, differences between these readings eliminate the unknown error and it is seen that the average potential between peaks is 4.85 volts. This agrees almost exactly with the energy differences, as found spectroscopically, between the lowest level $6s^2\ {}^1S_0$ and the first nonmetastable excited term $6s6p\ {}^3P_1$. The transition between these levels gives rise to the resonance line 2536.52 Å or 39,412.9 wave numbers which corresponds to 4.86 electron volts.

A slightly more complicated apparatus, also due to Franck and Hertz,[1] which contains an additional grid, is capable of higher resolving power and indicates many additional peaks corresponding to the values of other energy levels measured from the normal state when used at low gas pressures. Several of these critical potentials represent kinetic energy transfers for which the equivalent transition accompanied by radiation is not permitted. This shows that, although the atom can absorb kinetic energy only in the same discrete quantized amounts in which it can absorb radiation, nevertheless the selection rules applicable to the latter process do not apply at these kinetic energy transfers. Certain of these additional peaks can be observed with a thyratron with the mercury vapor pressure adjusted to about 6 mm., but the difficulty of observing

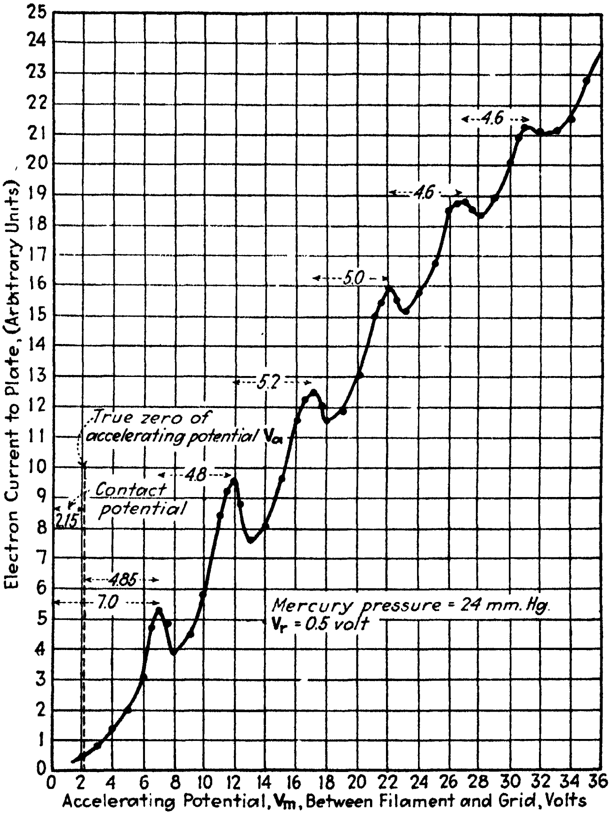

FIG. 8-10.—An inelastic impact curve obtained with an FG-27 thyratron, showing the lowest critical potential of mercury, at 4.86 volts. The circuit used was that of Fig. 8-9.

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[1] FRANCK and HERTZ, *Physik. Zeits.*, **17**, 409 (1916).

these maxima with a tube not designed for the purpose prevents satisfactory results. An ordinary screen-grid radio tube which has been opened to admit a few drops of mercury and then reevacuated, has the advantage of an extra control grid. The accelerating potential V_a is applied between the filament and the first grid, then a very small field (0.1 volt) continues to draw the electrons toward the second grid, between which and the plate the retarding potential V_r is applied. This arrangement has the advantage that there is a large, approximately field-free region between the grids in which electrons with the energy corresponding to V_a may collide; this greatly increases the resolving power of the apparatus. However, the grid spacings in an ordinary commercial tube are not the most favorable for this purpose, and as a consequence the curves of Franck and Hertz cannot be reproduced in detail. In endeavoring to measure these higher critical potentials it is a fundamental necessity that the temperatures of the tube and filament should be kept very constant; otherwise the slight variations in temperature, which greatly alter the recorded plate current, completely mask the small peaks.

A still more sensitive method, which may be used with a special tube, has also been devised by Hertz.[1] This method, which is indicated in Fig. 8-11, is capable of great precision and, furthermore, avoids the superposition of peaks that limits the sensitivity of the methods which have been previously described. Electrons from a filament are accelerated by a variable potential V_a through an opening into a field-free region where they collide with atoms of the gas or vapor. If the impacts are elastic, some of the electrons are deflected without loss of energy out through the sides of the gauze cylinder defining the field-free region and are able to advance against a retarding potential V_r of 0.1 volt between the gauze and a surrounding plate. As the accelerating potential V_a is increased in small steps, the current to the plate, as measured by a galvanometer, is observed both with $V_r = 0.1$ and $V_r = 0$; as long as the collisions are elastic the two galvanometer readings are approximately the same. When the potential is reached at which inelastic collisions first occur, the electrons lose practically all of their energy and retain an insufficient amount to reach the plate when the retarding potential of 0.1 volt is applied. Hence, at this potential, the galvanometer readings for the two values of V_r are found to differ, and this difference gives a measure of the number of electrons emerging from the gauze with energies less than 0.1 volt, *i.e.*, the number which have suffered inelastic collisions. Since the collisions occur in a field-free region, there is no possibility of an electron regaining energy from the field after an impact as in the original method, and repetitions of the same critical energy loss do not occur. Hence the contact potential may not be determined directly, but it may be inferred if one of the critical potentials is known or if a mixture of two gases is used for one of which the critical potentials are known.

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[1] HERTZ, *Zeits. Physik*, **18**, 307 (1923).

It is also possible to obtain further confirmatory evidence of stationary energy states by observing the optical effects produced by the excited atoms which are formed at these inelastic collisions. Every time an atom is excited by a collision with an electron it is in a position to return to its normal state by the emission of radiation, if the excited state is not metastable. This radiation may be detected by some suitable means. It has been observed photoelectrically by Franck and Einsporn,[1] using a tube similar to that described above containing two grids and a plate. The radiation emitted when an excited atom returns to its normal level falls on the plate and liberates a photoelectron; this photoelectric current from the plate is recorded by an electrometer. The radiation emerging from the region containing the excited atoms has also been observed directly by means of a spectrograph. Such observations have been made by a number of investigators, notably by Foote, Meggers, and Mohler[2] who have shown that one, two, three, and more spectral lines are produced as the energy of the bombarding electrons is successively increased through the values of the various excited states. As the technique is rather difficult and the necessary exposures very long, the detailed experimental procedure will not be given.

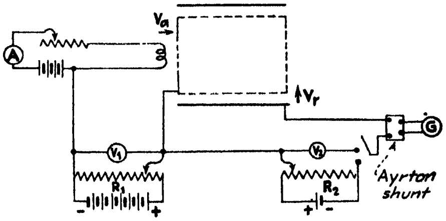

FIG. 8-11.—The Hertz method of detecting inelastic impacts of electrons with gas atoms.

8-10. Experiments on Ionization Potentials.—The determination of the critical electron energy necessary for the complete removal of an electron from an atomic system may also be made with the type of apparatus which has already been described. The simplest arrangement for measuring this ionizing potential in the case of mercury vapor is by the use of the thyratron which was previously employed for the measurement of the critical excitation potentials. It is merely necessary to transfer the plate lead in Fig. 8-9 from the grid to the filament, *i.e.*, connect the positive terminal of V_2 to the negative rather than the positive terminal of V_1. This maintains the plate 0.5 volt negative with respect to the filament for all values of the grid potential, thus preventing any electrons emitted by the filament from reaching the plate. Any positive ions formed in the region between the grid and plate are drawn to the latter electrode and are recorded by the galvanometer. For this observation the temperature of the furnace should be reduced till the vapor pressure of the mercury is about 0.5 mm. The galvanometer remains undeflected as the accelerating potential V_a of the electrons is increased until the ionizing potential is reached. At this point a few ions are formed near the grid, some of these are drawn to the plate, and the galvanometer is deflected in the direction indicating the reception of positive charges. The potential at which this occurs, as given by the voltmeter V_1, must be corrected for the contact potential between the electrodes as determined by the critical-potential measurements in order to obtain the true ionizing potential. This is found to be 10.4 volts which is in excellent agreement with the energy difference between the ground state $6s^2\ {}^1S_0$, and the ion as determined spectroscopically, which is 84,178.5 wave numbers or 10.39 electron volts.

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[1] FRANCK and EINSPORN, *Zeits. Physik*, **2**, 18 (1920).

[2] FOOTE, MEGGERS, and MOHLER, *Phil. Mag.*, **42**, 1002 (1921).

An alternative and extremely delicate method for detecting ionization potentials has been devised by Hertz.[1] Electrons from a filament F_1 are accelerated by a variable potential V_a into a field-free box where they collide with the atoms or molecules of the gas. The box contains a filament F_2 between which and the walls an accelerating potential V_b is applied. This potential is considerably less than the ionizing potential of the gas, and the filament is so hot that the current from it to the box is limited by space charge. As long as V_a is low enough so that the electrons from F_1 do not produce any ions in the box, the space-charge limited current as measured by a galvanometer remains constant, but when V_a is increased to such an extent that ions are formed, these neutralize some of the space charge around F_2 and the current through the galvanometer increases. The method does not permit any direct determination of the contact potentials between the electrodes, but by using two gases, for one of which the ionization potential is known, this additive constant may be determined.

A tube suitable for the measurement of both the excitation and ionization potentials by the Hertz methods is shown in Fig. 8-12. The electrical circuit in the figure is that for the measurement of ionization potentials; the circuit for excitation-potential measurements is given in Fig. 8-11; the second filament F_2 is connected to the gauze cylinder in the latter case. The two filaments pass through the presses on tungsten leads, nickel rods of suitable length are welded to these, and the filaments spot-welded across the ends. F_1 should be a coated platinum strip with a V-shaped notch in the center, in order to provide an approximately equipotential source; F_2 is an ordinary hairpin type filament of about 5-mil tungsten. The outer collecting cylinder fits snugly in the main part of the tube and the inner cylinder of nickel gauze is separated from it by two rings of Pyrex cane. These two electrodes are inserted before the filaments are sealed into place. The end of the gauze cylinder facing the filament F_1 is a nickel disk containing a gauze-covered opening immediately opposite the filament. The space between this opening and F_1 should be as small as possible, *i.e.*, of the order of 1 to 2 mm. The electrical connection to the inner cylinder may be made with a fine flexible helix of nickel wire spotted to a light tungsten rod for sealing through the wall; the sealing in is done after the electrode is in place. The connection to the outer cylinder can be made by a spring spotted to a tungsten wire sealed through the wall which presses against the outer surface of the cylinder. When the electrodes are all in place, the apparatus is sealed to a vacuum system and baked out at about 400°C. for several hours; during the process the filaments should be heated a little above the temperatures at which they are to be used. The tube is then ready for operation and the gas to be used is admitted at a pressure of a few millimeters of mercury. The optimum pressure depends on the gas and the exact electrode separations, and hence it must be found by trial. The types of curves obtained using the circuits of Figs. 8-11 and 8-12 are shown in Fig. 8-13 for neon. The abscissas are the voltages V_a (corrected for contact potentials), and the ordinates are the differences between the galvanometer currents for curve A, the peaks of which represent excitation potentials, and the current from the filament F_2 for curve B, the break in which indicates the ionization potential. As the contact potential between F_2 and the outer cylinder is not zero the abscissas of both curves must be corrected separately with a gas such as argon for which the excitation and ionization potentials are accurately known.

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[1] **Hertz,** *Zeits. Physik,* **18,** 307 (1923).

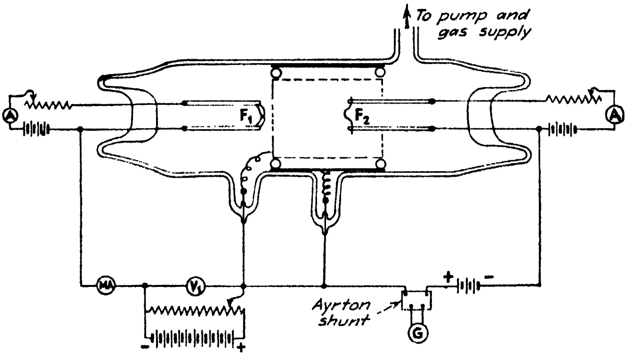

FIG. 8-12.—A diagram of an apparatus for the Hertz method of detecting ionization potentials of a gas. The tube indicated is also suitable for use with the circuit of Fig. 8-11 for measuring radiation potentials. For ionization-potential measurements the cylindrical grid and plate are connected together to act as a single electrode.

It should also be mentioned that the apparatus described in Chap. IV for the measurement of e/M for positive ions may be used for the measurement of ionization potentials. Let us assume for example that nitrogen is in the apparatus. The accelerating potential for the electrons from the filament is varied and the ion current reaching the Faraday collector,

TABLE OF EXCITATION AND SINGLE IONIZATION ENERGIES, IN ELECTRON VOLTS, FOR CERTAIN OF THE RARE GASES AND ALKALI METALS, AND FOR MERCURY

Element	Initial and final terms	Spectroscopic value	Electron bombardment value
Helium	$1s^2\ ^1S_0 - 1s2s\ ^3S_1$	19.73	19.75
	$- 1s2s\ ^1S_0$	20.56	20.55
	$- 1s2p\ ^1P_1$	21.12	21.2
	$- 1s3p\ ^1P_1$	22.98	22.9
	− ion	24.465	24.47
Neon	Excitation	....	16.6
	Excitation	....	18.5
	Ionization	....	21.47
Argon	Excitation	....	11.5
	Excitation	....	13.5
	Excitation	....	13.9
	Ionization	....	15.68
Sodium	$3s\ ^2S_{\frac{1}{2}} - 3p\ ^2P_{\frac{1}{2},\frac{3}{2}}$	2.093	2.12
	− ion	5.116	5.12
Potassium	$4s\ ^2S_{\frac{1}{2}} - 4p\ ^2P_{\frac{1}{2},\frac{3}{2}}$	1.603 and 1.610	1.55
	− ion	4.321	4.32
Rubidium	$5s\ ^2S_{\frac{1}{2}} - 5p\ ^2P_{\frac{1}{2},\frac{3}{2}}$	1.553 and 1.582	1.6
	− ion	4.159	4.16
Caesium	$6s\ ^2S_{\frac{1}{2}} - 6p\ ^2P_{\frac{1}{2},\frac{3}{2}}$	1.380 and 1.448	1.48
	− ion	3.877	3.88
Mercury	$6s^2\ ^1S_0 - 6s6p\ ^3P_0$	4.66	4.68
	$- 6s6p\ ^3P_1$	4.86	4.9
	$- 6s6p\ ^3P_2$	5.43	5.47
	$- 6s6p\ ^1P_1$	6.67	6.73
	$- 6s7s\ ^1S_0$	7.88	7.73
	$- 6s7p\ ^3P_{0,1}$	8.58	8.64
	$- 6s7p\ ^3P_2$ $- 6s7p\ ^1P_1$ $- 6s6d\ ^1D_2$ $- 6s6d\ ^3D_{1,2,3}$	8.78 to 8.82	8.86
	− ion	10.38	10.39

with the accelerating potential for the ions and the magnetic field set for some particular ion, say N_2^+, is plotted as a function of the electron-accelerating potential. The voltage at which this curve meets the axis of zero current to the collector gives the ionization potential (uncorrected for contact potentials) for that particular type of ion. These cut-offs are seldom sharp, but they can generally be estimated to a fraction of a volt. The great advantage of this type of apparatus is that in gases such as nitrogen where two types of ions, *i.e.*, N^+ and N_2^+, are formed, the potentials at which these different ions appear can be detected separately. Extensive discussions of the methods which have been used to measure excitation and ionization potentials and the results which have been achieved have been given by Compton and Mohler,[1] Franck and Jordan,[2] Kallmann and Rosen,[3] and Smyth.[4]

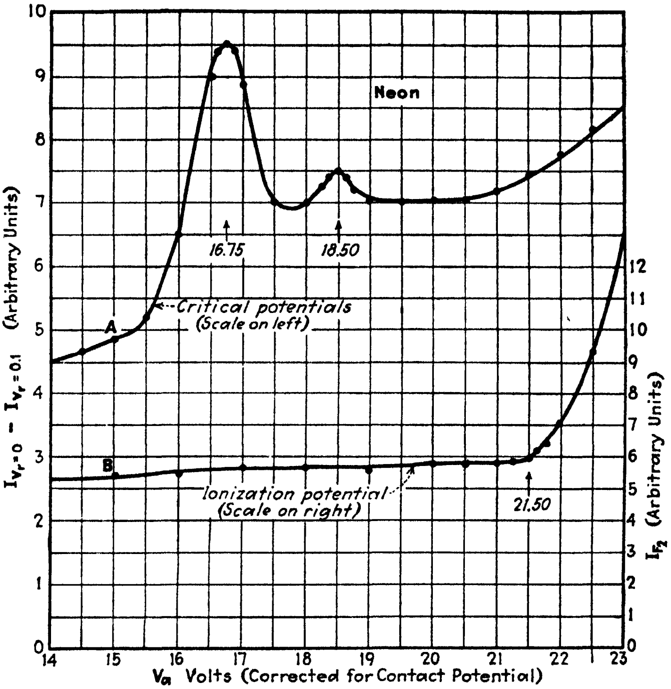

FIG. 8-13.—The radiation and ionization potentials of neon. The upper curve shows the radiation potentials found with the circuit of Fig. 8-11; the lower curve gives the ionization potential, using the circuit of Fig. 8-12. The abscissas are the accelerating potentials of the bombarding electrons, corrected for the contact difference of potential.

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[1] COMPTON and MOHLER, *Bull. Nat. Res. Council*, **9**, Part I, No. 48 (1924).

[2] FRANCK and JORDAN, "Anregung von Quantensprüngen durch Stösse," Springer (1926).

[3] KALLMANN and ROSEN, *Physik. Zeits.*, **32**, 521 (1931).

[4] SMYTH, H. D., *Rev. Mod. Phys.*, **3**, 347 (1931).

CHAPTER IX

X-RAYS

9-1. Introduction.—During the course of a series of experiments designed to investigate the radiation emitted by a discharge tube, Röntgen[1] observed in 1895 the presence of a type of radiation for which many materials, opaque to ordinary light, were transparent and which was capable of exciting fluorescence in substances, such as crystals of platinum-barium-cyanide, which fluoresce under the influence of ultra-violet light. The discharge tube was surrounded by a black-paper screen, but the radiation was able to cause fluorescence even through this material showing that it was much more penetrating than the types of radiation, such as visible and ultra-violet light, which had previously been known. Heavier materials, however, darkened the fluorescent screen when introduced between it and the discharge tube, showing that whatever it was which caused the fluorescence emanated from the tube and that it was capable of being absorbed or in some way intercepted by matter. These rays were named X-rays by Röntgen, and they are also sometimes known as Röntgen rays.

The discovery of these phenomena created a great deal of interest among investigators and many other important properties of the rays were soon observed. It was found that they emanated from those regions of the discharge tube which were bombarded by the cathode rays, *i.e.*, the electrons given off by the cathode, and it was also observed that the radiation was stronger if the electrons impinged on a heavy metal electrode rather than on the glass walls of the tube. If the region in which the X-rays were generated was small, so that it was effectively a point source, heavy objects interposed between the source and the fluorescent screen were observed to cast sharp shadows as in the case of opaque bodies and ordinary light. The fact that the rays were not deflected by electric or magnetic fields added further evidence to the growing conviction that they were of the nature of electromagnetic waves. They not only affected fluorescent screens but also photographic plates, and in addition they were observed to cause intense ionization in the air through which they passed. The last two characteristics provide the most convenient and accurate means for their detection.

These properties, namely, generation by electron bombardment, rectilinear propagation, independence of electric and magnetic fields, and absorption with the production of ionization, suggest very strongly that this radiation is electromagnetic in nature and closely analogous to visible and ultra-violet light. As it is excited by electrons which have fallen through a potential of several thousand volts, the radiation carries a great deal more energy with it than visible light, which can be generated by electrons that have fallen through a potential of only a few volts. This is in harmony with the fact that visible radiation when it is absorbed raises atoms to comparatively low excited states whereas X-rays possess sufficient energy to completely remove an electron even from the interior of an atom; in fact, by successive partial-absorption processes, to remove electrons from many atoms and produce intense ionization. If this interpretation of X-rays as electromagnetic radiation is correct we should expect that they would display the other phenomena associated with light such as reflection, refraction, diffraction, and polarization. From the relation $E = h\nu = hc/\lambda$, we see that, if the energy necessary to excite X-rays is of the order of a thousand times that necessary to excite visible light, their wave length is only about a thousandth that of light, namely of the order of 1 Å. This would make the phenomena of interference and diffraction much more difficult to observe than for visible light with ordinary slits or gratings.

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[1] RÖNTGEN, *Sitzungsber. der Würzburg. Ges.* (1895); *Ann. Physik*, **64**, 1 (1898).

9-2. Optical Properties of X-rays.—All of the typical wave phenomena have been observed for X-rays. Haga and Wind[1] directed a beam of X-rays through a wedge-shaped slit, less than 0.01 mm. wide at its broadest end, and observed the diffraction pattern produced on a photographic plate. As the separation of the diffraction maxima from the center should vary inversely as the slit width, a broadening of the pattern opposite the narrow end of the slit would be expected. This was observed. Later and more refined measurements by Walter and Pohl[2] established the fact that the wave length of the X-rays used by them was about 0.4 Å. This type of experiment has been performed more recently with monochromatic radiation and the wave-length estimates obtained agree very well with the wave length measured by other methods. The diffraction of X-rays by an ordinary ruled optical grating has also been observed,[3] and the measurement of wave lengths by this method gives probably the most convincing evidence that the interpretation of the wave nature of X-rays is correct. An excellent review of the diffraction phenomena which have been observed with X-rays has been given by Bäcklin.[4] A measurement with a grating yields an absolute value for the wave length since the grating constant can be directly measured. These values agree to within about 0.25 per cent with the wave lengths measured by means of a crystal lattice grating. The principle of wave-length measurement with a crystal grating has been described in Chap. V, and its use with X-rays will be discussed later in this chapter. Though the wave lengths as measured by these two methods, *i.e.*, ruled gratings and crystals, are very nearly the same, indicating the general correctness of our conceptions, they do not accurately agree to within the limits of error of the two methods. An apparently real and unexplained discrepancy exists at present between the wave lengths determined in these two ways. The work of Bearden[1] has clearly outlined the problem thus presented, but it is not yet evident to which element or elements of the grating or crystal measurements the error is to be assigned.

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[1] Haga and Wind, *Wied. Ann.*, **68**, 884 (1899).

[2] Walter and Pohl, *Ann. Physik*, **25**, 715 (1908); **29**, 331 (1909).

[3] Doan and Compton, A. H., *Proc. Nat. Acad. Sci.*, **11**, 598 (1925).

[4] Bäcklin, Dissertation, Uppsala (1928).

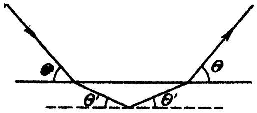

FIG. 9-1.—The refraction of a beam of X-rays in a crystal, for which the index of refraction is less than unity.

It was during the course of an accurate investigation by Stenström[2] of the angle of diffraction of X-rays of comparatively long wave length (greater than 3 Å) that the first direct evidence of the phenomenon of refraction was observed. Stenström found that the observed diffraction maxima did not accurately obey the Bragg relation:

$$n\lambda = 2d \sin \theta \qquad (9\text{-}1)$$

[Eq. (5-35)], where λ is the wave length in air, and θ is the angle between the incident X-rays and the Bragg reflecting plane. If the velocity of propagation of the X-rays in the crystal is not equal to their velocity in the region outside, we have by Snell's law:

$$\mu = \frac{\cos \theta}{\cos \theta'}$$

where μ, the index of refraction, is equal to v/v', the ratio of the velocities, or λ/λ', the ratio of the wave lengths in the two media. Assuming that the Bragg relation holds inside the crystal, *i.e.*,

$$n\lambda' = 2d \sin \theta'$$

and eliminating $\sin \theta'$ and λ' by the relations

$$\sin \theta' = \sqrt{1 - \cos^2 \theta'} = \sqrt{1 - \frac{\cos^2 \theta}{\mu^2}} = \sqrt{\frac{\sin^2 \theta - (1 - \mu^2)}{\mu^2}} = \frac{\sin \theta}{\mu}\sqrt{1 - \frac{(1 - \mu^2)}{\sin^2 \theta}}$$

and

$$\lambda' = \frac{\lambda}{\mu}$$

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[1] BEARDEN, *Phys. Rev.*, **37**, 1210 (1931); **39**, 1 (1932).

[2] STENSTRÖM, Dissertation, Lund (1919).

we obtain

$$n\lambda = 2d \sin \theta \sqrt{1 - \frac{(1 - \mu^2)}{\sin^2 \theta}}$$

As the index of refraction is found to differ very little from unity, we may write the difference $1 - \mu$ as δ and expand the radical, neglecting terms in δ^2, giving

$$n\lambda = 2d \sin \theta \left(1 - \frac{\delta}{\sin^2 \theta}\right) \tag{9-2}$$

With this additional parameter δ, the observed data by Stenström and by Duane and Patterson,[1] and others, can be accurately represented and the value of δ, or the index of refraction $\mu = 1 - \delta$, can be calculated from the measurement of the angle θ for the same wave length in two orders. The index of refraction is found to be less than unity (as indicated in Fig. 9-1) by an amount of the order of 10^{-6}. This is in good qualitative agreement with the predictions of elementary dispersion theory for radiation, the frequency of which is high in comparison with the natural frequency of the electrons in the substance.

The fact that most materials have an appreciable index of refraction for X-rays and that it is less than 1 is of vital importance in the use of a ruled grating. As $\mu < 1$, $\cos \theta < \cos \theta'$ or $\theta' < \theta$. When $\theta' = 0$, θ still has a finite positive value, θ_0. Hence for angles of incidence between θ_0 and 0 there can be no refraction and the X-rays are totally reflected from the surface. This phenomenon was first observed by Compton[2] and it suggested the use of a ruled grating at very small angles of incidence for wave-length measurements. If the X-rays strike the surface at less than the critical angle they are totally reflected, and the intensity in the observed diffraction pattern becomes very large. Thus the experimental arrangement for grating measurements is, in general, similar to that described in Chap. V for the measurement of the effective wave length of a beam of electrons by a grating (see Fig. 5-3).

It was found that the critical angle for total reflection, and hence the refractive index, was different for different wave lengths. Therefore it would be expected that the phenomenon of dispersion, so familiar in the case of visible light passing through a glass prism, could be observed. However, as the index of refraction is small the rays are deviated very little, and as it is less than 1 the refracted beam is bent in the opposite direction to that of visible light. The deviation of a beam of X-rays on passing through a prism, and also the dispersion of this beam into a spectrum, was first observed by Larsson, Siegbahn, and Waller.[3] The

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[1] Duane and Patterson, *Phys. Rev.*, **16**, 526 (1920).

[2] Compton, A. H., *Bull. Nat. Res. Council*, No. 20, p. 48 (1922).

[3] Larsson, Siegbahn, and Waller, *Naturwiss.*, **52**, 1212 (1924); *Phys. Rev.*, **25**, 235 (1925).

X-ray beam was directed on to the extreme tip of a prism and at an angle only slightly greater than the critical angle for total reflection. Certain of the characteristic lines in the X-ray spectrum of copper and iron were actually observed separately, although the angular deviation was only of the order of a few minutes of arc. Although the dispersion of X-rays by a prism is not so useful a means for their investigation as the similar phenomenon in the case of visible light, it yields very important evidence as to the mechanism of dispersion and may be used as an auxiliary method of wave-length determination. A complete discussion of the phenomenon of X-ray dispersion has been given by Larsson.[1]

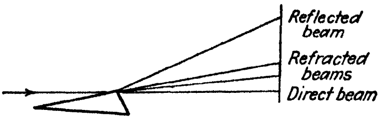

FIG. 9-2.—The refraction of X-rays by a prism.

The phenomenon which probably shows most directly the vectorial nature of electromagnetic waves is that of polarization. It is very familiar in the region of visible light, for reflection, transmission through crystals, and scattering tend to produce a resultant beam with properties which are not symmetrical about the axis of propagation. When a beam is completely polarized by one of these methods, a preferred direction exists perpendicular to the direction of propagation which is associated with either the electric or magnetic vector of the wave. Thus in the familiar Nörrenberg polariscope, light is reflected from a mirror, which is set at the critical angle for complete polarization, to a second mirror capable of rotation about the axis of the light incident upon it. When the second mirror is parallel to the first, it reflects light with this plane of polarization; but when rotated through 90°, this light is not reflected and the mirror appears dark to an observer.

A very similar type of experiment was tried by Barkla[2] with X-rays. His results showed a large percentage polarization of the rays which had been scattered from a carbon block. The experimental arrangement for detecting this polarization is shown diagrammatically in Fig. 9-3. Comparatively unpolarized X-rays leaving the anticathode of the tube T impinge on a scattering block A. The vectors representing the amplitudes of the waves are symmetrically distributed about the line joining T and A which is taken as perpendicular to the plane of the paper. If we now consider that we are observing the radiation scattered along the line AB, in the plane of the paper, to an observer at B all the vectors representing wave amplitudes would apparently lie in this plane, since they all were originally perpendicular to TA. Thus the X-rays from A to B on this simple conception would be expected to be polarized in the plane of the paper. We now use a second scattering block at B as an analyzer and observe, in a direction parallel to TA, the radiation reaching an ionization chamber at C. As the waves from A to B are polarized in the plane of the paper, the waves along BC will be polarized in a plane perpendicular to AB. If, on the other hand, we rotate the ionization chamber 90° around AB to C' (BC' perpendicular to BC and to AB), there is no vector amplitude perpendicular to the direction of observation. Hence no X-rays should be observed along BC' if this mechanism is correct, and this is in agreement with experiment. Measurements by Compton and Hagenow,[1] in which the scattering blocks were reduced in thickness until multiple scattering was negligible and in which the proper allowance was made for the fact that the radiation was not strictly parallel, have shown that the polarization of the scattered radiation along AB is complete to within an experimental error of less than 2 per cent.

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[1] LARSSON, Dissertation, Uppsala (1929).

[2] BARKLA, *Nature*, *Mar.* 7 (1904); Mar. 9 (1905); *Phil. Trans. Roy. Soc*, **204**, 467 (1905); *Proc. Roy. Soc.*, **77**, 247 (1906).

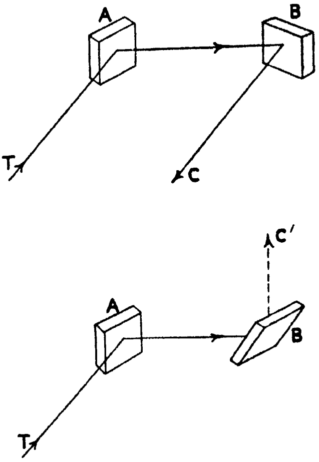

FIG. 9-3.—The polarization of X-rays.

Thus all these phenomena which we have considered have shown the complete qualitative similarity between visible light and X-rays. On the basis of these experiments we are justified in treating X-rays exactly as we did photons with smaller associated frequencies, and we may conceive of them also as packets of energy of amount $h\nu$ traveling with a velocity approximately equal to c (strictly equal to c when $\mu = 1$) and guided in their trajectory by the electromagnetic wave field. Where the electromagnetic intensity is large, there is a correspondingly large probability of observing the effect of a photon, such as the production of an ion or the activation of a silver grain on a photographic plate. The differences between X-rays and visible light are of degree rather than of kind and are all attributable to the extremely short wave length or the very large energy associated with an X-ray photon. Our main interest in the subsequent discussion of them will be in the information they yield of the fine structure of crystalline matter because of their very short wave length and in the extension of our knowledge of atomic spectra to those innermost states in heavy atoms which have very large negative potential energies.[2]

[1] COMPTON, A. H., and HAGENOW, *J. Optical Soc. Am.*, **8**, 487 (1924).

[2] COMPTON, A. H., "X-rays and Electrons," Van Nostrand (1926).

SIEGBAHN, "Spectroscopy of X-rays," Oxford University Press (1925); "Spektroskopie der Röntgenstrahlen," Springer (1931).

KIRCHNER and LINDH, *Handbuch der Expt. Physik*, vol. XXIV (1930).

9-3. Production of X-rays.—The essential apparatus for the generation of X-rays is a high potential source and an evacuated tube in which electrons may be accelerated toward a massive electrode. The potential difference applied to the tube determines the so-called "hardness" or penetrating power, strictly, by Einstein's equation $eV = h\nu$; the potential determines the highest possible frequency or shortest wavelength radiation which can be obtained from the tube. From the above expression we see that λ in Ångström units is related to V in volts by the relation

$$\lambda = \frac{c}{\nu} \times 10^8 = \frac{hc}{eV} \times 300 \times 10^8 = \frac{12{,}336}{V}$$

Thus for a voltage of 12,336 X-rays of wave length equal to, and longer than, 1 Å can be obtained, while to obtain "harder" X-rays, with a wave length equal to 0.1 Å, a potential of about 125,000 volts must be employed. For ordinary X-ray work, such as that to be described later in this chapter, a potential source of from 50,000 to 100,000 volts is satisfactory.

To obtain sufficient intensity currents of several milliamperes must be used, hence the transformer should have a rating of several kilovolt-amperes. Satisfactory results may be obtained with old medical X-ray units, or the small units rated at 4 kva., manufactured by the General Electric X-ray Corporation, are very convenient for this type of work. These medical units generally contain a mechanical rectifier whose operation is indicated in Fig. 9-4. It consists of a fiber or micanite disk carrying two electrodes, mounted on the shaft of a synchronous motor. This disk rotates between four fixed electrodes, two from the transformer and two from the X-ray tube, in such a way that each transformer terminal is connected alternately to each of the tube electrodes during every alternating-current cycle. Thus pulsating direct current is supplied to the X-ray tube. The correct adjustment of the rotating electrodes with reference to the fixed ones can best be made by observing the current through the tube for various settings of the micanite disk relative to the synchronous motor armature. When this adjustment has been properly made, the current through the tube is a maximum. While this type of rectifier can be used satisfactorily, it has the disadvantage that the potential supplied to the tube is pulsating and that the wave form is very irregular.

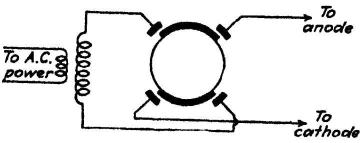

FIG. 9-4.—A mechanical rectifier, driven by a synchronous alternating-current motor, for an X-ray tube.

If a standard unit is not to be used it is advisable to obtain an X-ray transformer with a 4- or 5-kva. rating, together with an autotransformer or resistance regulator and to rectify the output with thermionic tubes (kenotrons). These of course can be used without condensers, just as they can be dispensed with entirely and the X-ray tube itself allowed to perform the function of rectification, but these arrangements are unsatisfactory as a large fraction of the current which heats the target flows in those portions of the cycle during which the potential is too low to generate any useful X-rays. More satisfactory circuits employing one or two rectifying tubes are shown in Fig. 5-14. These employ condensers to store electric charge between cycles so that an approximately constant potential is maintained across the X-ray tube. The magnitude of potential variation with such an arrangement was discussed in Chap. V [Eq. (5-43)]. It is inversely proportional to the frequency of the alternating current, hence when a very constant potential is desired, it is advisable to use a motor-generator set with a high-frequency output (500 cycles or greater) to excite the X-ray transformer. However, for most purposes it is unnecessary to have a very constant potential and the ordinary 60-cycle current may be used with a capacity of a few hundredths of a microfarad, if the tube current does not exceed 10 or 20 milliamp. These capacities can be purchased or they may be built up of banks of glass plates with metal-foil electrodes shellacked on either side. A good glass will withstand a difference of potential of 50,000 volts per millimeter thickness, but for safety only about a half or a third of this gradient should be used. Taking the dielectric constant of glass to be about 5, ten sheets of glass 20 in. square and $\frac{1}{8}$ in. thick with electrodes extending to within 3 in. of each edge, arranged in parallel, have a capacity of about 0.03 μf., which is adequate for ordinary purposes. The simplest circuit, as in *A*, Fig. 5-14, employs but one rectifying tube and utilizes only half the cycle. The kenotron must be capable of withstanding twice the potential applied to the X-ray tube, as during the unused half of the cycle the filament becomes almost twice the transformer voltage negative with respect to the plate. Circuit *B*, Fig. 5-14, employing two tubes, applies twice the transformer voltage to the X-ray tube and the kenotrons must also be able to withstand this voltage; the potential fluctuation across the tube is about twice that of circuit *A*, *i.e.*, about the same percentage of fluctuation as in that arrangement.

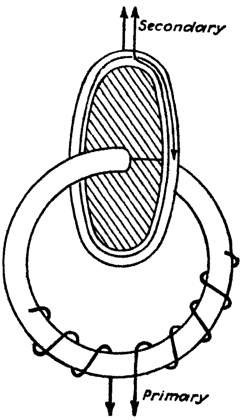

FIG. 9-5.—A filament transformer for an X-ray tube or kenotron.

Properly insulated transformers for lighting the filaments of the X-ray tube and kenotrons can be purchased as regular X-ray equipment or they may be constructed very simply. A core in the form of a ring about

2 ft. in diameter and about 1 sq. in. in cross section is built up of strips of transformer iron. This should be bound tightly together with friction tape and wound with about 300 or 400 turns of No. 18 insulated wire. This is the primary and is connected through a regulating rheostat of about 50 ohms with the 60-cycle mains. The secondary should have from 30 to 60 turns of about No. 14 insulated wire depending on the rated voltage of the filament of the tube; these turns should be about 2 ft. in diameter bound with tape and linked with the transformer core as shown in Fig. 9-5. The primary and secondary coils may be supported by a frame of shellacked or paraffined wood, or the secondary may be wound upon a split disk of bakelite which clamps tightly on to the core as shown in the illustration. If rigidity is not required, the primary may be mounted on a wooden support and the secondary simply suspended from the insulating frame supporting the cathode end of the tube.

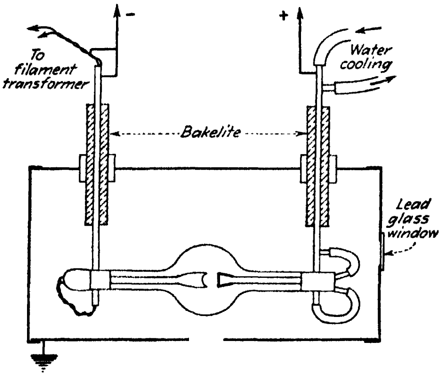

FIG. 9-6.—The details of a lead housing for an X-ray tube.

Methods of measuring high potentials were discussed in Chap. V; of these the simplest is the sphere gap, which is sufficiently accurate for most purposes. A table of sparking potentials was given in connection with that discussion. Various designs of electrostatic voltmeters, as more accurate instruments for potential measurement, and many other important items of technique are given by Terrill and Ulrey[1] and Clark.[2] A milliammeter with a range of 20 or 30 milliamp. should be included in the secondary circuit; this may advantageously be shunted by a condenser or a small needle gap to protect the meter from high-frequency surges. Furthermore, if a gas-filled X-ray tube is to be used, a high protective resistance (wire-wound type) should be included in the circuit between the transformer and the potential-measuring device. The wiring should be done with fairly heavy conductors such as No. 10 or 12 copper wire, both for structural rigidity between supports and to reduce corona

[1] TERRILL and ULREY, "X-ray Technology," Van Nostrand (1930).

[2] CLARK, "Applied X-rays," McGraw-Hill (1932).

loss. These high-potential leads should be protected if possible with wire-mesh screening, which is grounded, to guard against any accidental contact with them. The connections to the tube may pass into the lead shielding box through large bakelite bushings. If the anode is water cooled, the connection through the bushing is conveniently a double-walled copper tube which also carries the water stream to the target and away from it. If the anode is at a high potential, the rubber tubes for carrying this water should be 15 or 20 ft. long to avoid excessive loss through them to the ground. The other connection to the tube may also be a copper tube carrying the heating leads to the filament. The lead box itself should be large enough so that there is no danger of breakdowns between the electrodes and the walls of the grounded box, and also so that there is room enough to reach in and make the necessary tube adjustments. In order to obtain the greatest intensity of X-rays, the tube should be placed so that the anode is as close to the window of the box as can be done with safety. A cylindrical lead box about 3 ft. long and 18 in. in diameter with removable ends, which has been used satisfactorily together with the auxiliary arrangements is shown in Fig. 9-6. The thickness of lead necessary for complete protection varies with the wave length of the X-rays, *i.e.*, with the applied voltage. The following thicknesses have been specified by the English X-ray and Radium Protection Committee:

Voltage in Kilovolts	Minimum Thickness of Lead in Millimeters
70	1.5
100	2.0
150	3.0
200	4.0

To insure that sufficient protection has been provided, a small dental X-ray film, with a metal clip on it by which to judge the blackening, may be carried in the pocket. This should not show any well-defined image of the clip upon development after about two weeks of work.

The most satisfactory type of tube for general work in X-ray analysis and crystal structure is one of the Coolidge type (hot filament) with a water-cooled molybdenum target imbedded in a heavy copper anode, such as is manufactured by the General Electric X-ray Company. This tube can be operated continuously at approximately 1 kva. (25 milliamp. at 30 kv. effective) and yields a sufficiently intense continuous spectrum as well as very intense lines of the *K* series of molybdenum. A tube with a tungsten target has the advantage of a higher melting point for the target material, and hence there is less sputtering or evaporation for the same energy dissipation, but the characteristic radiation which lies in a convenient wave-length range (the *L* series) is in general less intense than the molybdenum *K* lines. Such a tube with a tungsten target is more satisfactory for higher voltage ranges. The Coolidge type of tube, in which the cathode is a hot filament and in which the vacuum conditions are as good as can be obtained, has the advantage of requiring practically no attention and the possibility of independent control of both the quantity and quality of the X-rays emitted. The current through the tube which controls the output intensity can be adjusted by varying the temperature of the filament without appreciably altering the voltage across the terminals, which, together with the material of the target, determines the distribution of energy in the spectrum. A more intense source of radiation, which is a great advantage for certain methods of crystal analysis, is furnished by a gas-filled tube. The old type of gas tube which is permanently sealed from the pumping system is unsatisfactory, as it is very unstable in operation. Recently, however, several types of gas-filled tubes, permanently connected to a vacuum system, have been developed by Shearer, Siegbahn,[1] and others. Some of these tubes are for direct-current operation and others are self-rectifying. For stable operation a gas-pressure regulator such as described by Siegbahn or Wyckoff[2] must be included in the system. This complicates the experimental arrangements and as a consequence it is hardly to be recommended for elementary work. The intensity of the radiation emerging from such a tube under favorable conditions is so great that crystal-diffraction pictures can be taken in about a tenth the time required with the Coolidge type of tube. The Shearer design of gas-filled tube is manufactured by Adam Hilger and Company, London.

9-4. X-ray and Crystal Analysis.—The first step in the detailed analysis of crystal structure, which opened the way to the analysis of X-radiation, was due to a suggestion of von Laue. On his advice Friedrich and Knipping[3] directed a narrow pencil of X-rays upon a crystal of zinc blende ($\beta - \text{ZnS}$), behind which was placed a photographic plate. After several hours' exposure, the plate was developed and showed a series of blackened spots arranged symmetrically about the very intense central image. It was found that these spots lay in the arrangement that would be predicted for the scattering or diffraction of electromagnetic waves from a cubic-space lattice. Thus a complete explanation of the phenomena was provided upon the eminently reasonable lattice-structure theory and it can be seen that a method was established by this one experiment both for the analysis of crystal structure and for the spectral analysis of X-rays.

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[1] SIEGBAHN, "Spectroscopy of X-rays," Oxford University Press (1925); "Spektroskopie der Röntgenstrahlen," Springer (1931).

[2] WYCKOFF, "The Structure of Crystals," p. 60, Chemical Catalog Company (1931).

[3] FRIEDRICH, KNIPPING, AND VON LAUE, *Sitzungsber. der Bayer. Akad. Wiss.*, p. 311 (1912); *Ann. Physik*, **41**, 971 (1913).

This original experiment was followed immediately by the work of W. H. and W. L. Bragg[1] who introduced the rotating crystal method of analysis and the conception of reflecting crystal planes as described in Chap. V. Upon these two fundamental researches the science of crystal analysis and the study of X-rays are based. These methods and their variants, which have subsequently been introduced, provide all the information necessary for the analysis of crystals. The rotating crystal method disperses a beam into a spectrum in a very similar way to that in which a fixed ruled grating spreads the wave lengths present in a beam of light into a spectrum. We shall now consider three standard procedures for the analysis of X-rays and crystal structure. We shall deal only with the simplest crystal classes. For a complete account of the application of X-rays to crystal analysis, reference should be made to the treatises of Wyckoff, Schleede and Schneider[2] or Niggli, Ott, and Hertzfeld.[3]

9-5. Laue Spots.—Photographs of Laue spots can be taken with very simple apparatus. An arrangement which has been found satisfactory is shown in Fig. 9-7; an alternative set-up adapted for use with small crystals and when the crystal is to be accurately oriented, is described by Wyckoff.[4] A heavy-walled brass cylinder about 15 cm. long, held by a set screw in a heavy collar attached to the base plate of the apparatus, supports at either end two lead disks 3 or 4 mm. thick, through the centers of which the defining pinholes are bored with a No. 60 drill. The utility of the apparatus is increased if these lead diaphragms are removable from the supporting tube, so that they may be replaced by slits for other types of work. A disk-shaped lead shield through which this cylinder passes fits against the lead box containing the tube when the front pinhole at *A* is as close to the X-ray tube target as possible. The optimum adjustment for intensity of the collimated X-rays is made by viewing the beam with a fluorescent screen while the tube is in operation. The intensity is greatest if the X-rays reaching the pinholes leave the target face at a small angle. The crystal to be examined is supported over a hole in the shield *C*. This may be of heavy brass sheet, or all three diaphragms

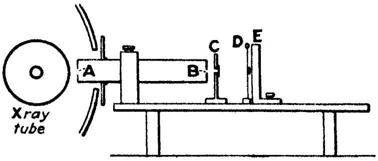

Fig. 9-7.—An experimental arrangement for obtaining Laue spots.

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[1] Bragg, W. H. and W. L., *Proc. Roy Soc.*, **88**, 428 (1913); **89**, 246, 248 (1914).

[2] Schleede and Schneider, "Röntgenspektroskopie," deGruyter (1929).

[3] Niggli, Ott, and Hertzfeld, *Handbuch der Expt. Physik*, vol. VII (1928).

[4] Wyckoff, "The Structure of Crystals," p. 125, Chemical Catalog Company (1931).

A, *B*, and *C* may be made of one of the numerous lead-copper-zinc or lead-antimony alloys which are readily machined. The hole in *C* should be just large enough so that the slightly divergent beam leaving *B* will not strike its edges; it then acts as a screen for the radiation scattered from the preceding diaphragm. If the crystal is large and a picture normal to a cleavage face is desired, it may be waxed or cemented directly over the hole in *C*. If, on the other hand, it is very small, it can be fastened with Duco cement to a thin piece of glass or celluloid which in turn is mounted over the hole in *C*. The best thickness of crystal to use depends on the tube voltage and the absorption coefficient of the crystal. For a voltage of 50 or 60 kv., crystals similar to those of sodium or potassium chloride give satisfactory results when they are about 0.5 mm. thick. These specimens may be prepared by cleaving, *i.e.*, by gently tapping a sharp edge placed along a cleavage plane, or by grinding if special faces are desired. In the case of soluble crystals such as sodium or potassium chloride, the crystal may be reduced in thickness by rubbing on wet silk stretched over a piece of plate glass, as described in Sec. **2-11** for the polishing of rock-salt prism faces. A 5 by 7 in. photographic plate is supported at *E* by a frame plate holder which is screwed to the base plate a short distance behind *C*. A separation *CE* of about 4 cm. is satisfactory for most purposes. If possible this distance *CE* should never be changed for Laue spot pictures, for, if this is always the same, a permanent set of reduction tables involving this distance may be prepared. A heavy-wire or strip-metal frame at *D* about the size of the photographic plate supports two or more threads intersecting on the X-ray beam, and at their intersection is waxed a lead disk 2 or 3 mm. thick and 0.5 cm. in

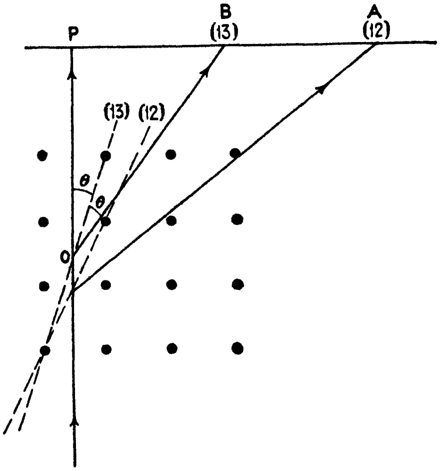

FIG. 9-8.—A section through a (100) plane in a cubic crystal, indicating the reflection of an X-ray beam from two Bragg planes.

diameter. This protects the plate from the direct X-ray beam, which would otherwise produce intense halation, for all but a few minutes of the exposure. The proper adjustment of the threads and disk may be made with a fluorescent screen while the tube is in operation. The plate or film is wrapped in black paper to protect it from visible light and placed in the holder. Exposures of about 10 or 20 milliamp.-hr. are satisfactory for average crystal specimens. Either plates or front- and back-coated X-ray film may be used. As the radiation from the tube is unfiltered, a large range of wave lengths is present in the beam.

The photographs obtained resemble those of Figs. 9-11, 9-12, and 9-15; the next question is their interpretation and the information which this yields as to the nature of the crystal. From the discussion of crystal structure in Chap. V we see that we should expect strong maxima for those angles of deviation from the beam equal to 2θ, where half this angle of deviation or the angle of incidence on the effective Bragg plane, θ, is given by [Eq. (5-35)]

$$n\lambda = 2d_{hkl} \sin \theta \tag{9-3}$$

where the possible values of d_{hkl} are given by:

$$\text{Cubic crystals, } d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{9-4}$$

$$\text{Orthorhombic crystals, } d_{hkl} = \frac{1}{\sqrt{\dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{l^2}{c^2}}} \tag{9-5}$$

Figure 9-8 represents a two-dimensional plane, a section through a (1 0 0) plane of a cubic crystal, containing the X-ray beam. For certain wave lengths present in the beam the Bragg relation [Eq. (9-3)] will be satisfied for the planes indicated by dotted lines, and diffraction maxima will appear at A, B, etc., and at corresponding intervals on the other side of P. From the distance of these spots from the direct image P, the Bragg angle can be determined, for from the diagram it is seen that

$$\frac{BP}{OP} = \tan 2\theta \tag{9-6}$$

Similar two-dimensional sections through the crystal in different azimuths, which contain the incident X-ray pencil and which are perpendicular to Bragg planes, may be drawn, and the diffraction spots to be expected in these planes predicted. The dark spots on the photographs correspond to all the more intense diffraction beams to be anticipated from this family of planes containing the OP-axis.

The most convenient method of interpreting these spots is by means of *gnomonic projection*. The principle of this projection is shown in Fig. 9-9, which represents a section through the crystal containing the OP-axis and perpendicular to a set of Bragg planes. The line OQ' indicates the continuation of the intersection of a Bragg plane with the plane of the figure, the line OQ'' is the perpendicular to this plane through O, and the solid lines are the directions of the X-ray beams. If, for example, the diffracted beam Q corresponds to the "reflection" from an (0 2 1) plane of a crystal with rectangular axes (the incident X-ray beam lying along the z-axis), Q' represents the intersection of the (0 2 1) plane with the plane of the paper and the photographic plate. The distances OP and PQ' are in the ratio of the intercepts of the plane with the z- and y-axes, or in the inverse ratio of the Miller indices 2 and 1. Hence:

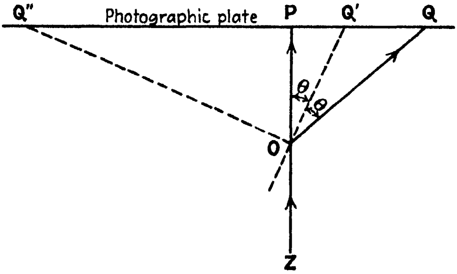

FIG. 9-9.—The point Q'' is the gnomonic projection of the point Q.

$$\frac{OP}{PQ'} = \frac{c/1}{b/2} = \frac{2c}{b}$$

where c and b are the unit lengths along the z- and y-axes, respectively. As OQ'' is perpendicular to $O\,Q'$, we have

$$\frac{PQ''}{OP} = \frac{OP}{PQ'}$$

or

$$PQ'' = OP\frac{2c}{b}$$

Hence considering the series of planes of the form (0 k 1), the intercepts of their normals with the plate will be at distances equal to $k(c/b)OP$ from the central image. Analogously, in the plane perpendicular to the paper containing OP, the intercepts of the normals to the series of planes of the form (h 0 1) will lie at distances $h(c/a)OP$ from the central image (a being the unit distance along the x-axis). Thus the intercepts of the normals of planes of the form ($h\,k$ 1) will form a rectangular network whose unit distances are inversely proportional to the parallel unit distance of the crystal. A measurement of these network distances for a crystal with rectangular axes (the X-rays being incident along one axis) yields the ratio of the unit lengths along the crystal axes with the proper choice of h and k, but it does not yield the values of these unit dimensions. The proper choice of the indices h and k is immediately evident in a cubic diagram; for crystals of lower symmetry the intensities of the spots and their relation to the intensities of the different wave lengths in the primary beam serve to determine this point. For a cubic crystal the gnomonic network is square. In general with an arbitrary crystal type or with a rectangular type for which the incident X-rays are not along one of the axes, the correct Miller indices are not as easily assigned. For a detailed discussion of the analysis of Laue patterns the reader is referred to the treatises on crystal structure.[1]

The actual process of gnomonic projection is most conveniently done with a so-called gnomonic ruler. The projection of a spot lies on the extended line joining the spot and the central image, and at such a distance beyond P that $Q'OQ''$ is a right angle. We have the relations

$$\begin{aligned} \frac{PQ}{PO} &= \tan 2\theta \\ \frac{PQ''}{PO} &= \tan (90^\circ - \theta) = \cot \theta \end{aligned} \qquad (9\text{-}7)$$

where PQ is the distance from the central image to the spot and $Q''P$ is the distance from the gnomonic projection of the spot to the central image. Hence, if a double ruler, as shown in Fig. 9-10, is constructed, one

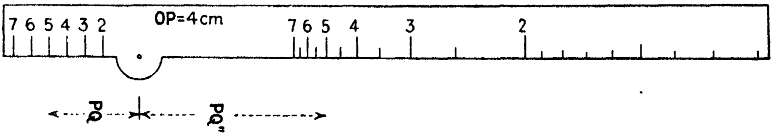

FIG. 9-10.—A gnomonic ruler.

side being divided in millimeters (for reading PQ) and the other side being divided in the corresponding intervals $Q''P$ by the parametric Eqs. (9-7), then, when the center of the ruler is placed over the central image and the millimeter scale is on a Laue spot, the gnomonic projection lies under the corresponding division of the $Q''P$ scale. If the distance OP is chosen equal to 4 cm., the table of values of the divisions on either side of the ruler and the corresponding value of sin θ given by Wyckoff[2] may be used in the construction of the ruler. Otherwise a similar table must be constructed from Eqs. (9-7). A positive print of the Laue picture on a process film is most convenient for making a gnomonic analysis. It is fastened in the center of a large sheet of white paper by pins or wax at the corners, and a pin through both the center of the ruler and the direct image acts as the axis about which the ruler is revolved. As each spot is recorded a notation of the corresponding angle θ and the estimated intensity should be made. These are of particular importance in the assignment of the correct unit crystal cell for crystals of lower than cubic symmetry.

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[1] WYCKOFF, "The Structure of Crystals," Chap. VI, Chemical Catalog Company, (1931).

SCHLEEDE and SCHNEIDER, "Röntgenspektroskopie," deGruyter (1929).

NIGGLI, OTT, and HERTZFELD, *Handbuch der Expt. Physik*, vol. VII (1928).

[2] WYCKOFF, "The Structure of Crystals," p. 131, Chemical Catalog Company (1931).

Figures 9-11 and 9-12 are Laue photographs of sodium chloride and potassium chloride, respectively, perpendicular to their cleavage faces.

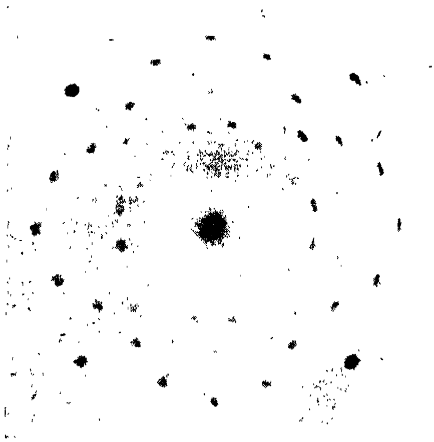

FIG. 9-11.—The Laue spots obtained with sodium chloride.

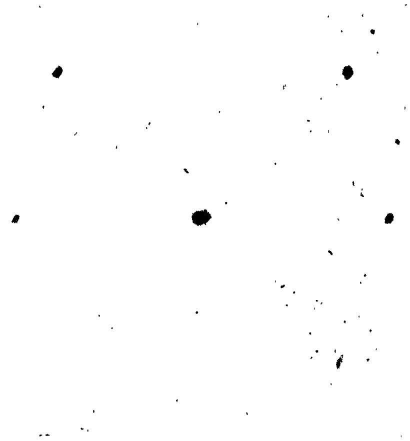

FIG. 9-12.—The Laue spots obtained with potassium chloride.

The same type of symmetry is evident in both photographs, and identical pictures would have been obtained if the X-rays had been incident on either of the other two cleavage planes. The gnomonic projection of the visible spots in Fig. 9-11 is shown in Fig. 9-13 and from this the cubic symmetry of the crystal is obvious. The original photograph shows many other faint spots farther from the center whose gnomonic projections do not lie on intersections of the index lines. These correspond to the planes ($hk2$), ($hk3$), etc., which are not essential for our purposes. The most striking difference between Figs. 9-11 and 9-12 is in the relative intensities of the spots. In Fig. 9-11 (NaCl) the spots corresponding to intersections of the odd index lines are relatively much more intense than in Fig. 9-12 (KCl) in which even the $h = 3$ and $k = 3$ intersection is scarcely visible in the reproduction. The intensity of similar spots from crystals of the same structure is a measure of the number of atoms in the reflecting planes, if the intensity of radiation of the proper wave length to give rise to the spots is approximately the same for both: that is, other things being equal, we may consider that an intense spot corresponds to a thickly populated plane. If the crystal is a simple cubic type with identical atoms at each lattice point, the number of atoms per plane is proportional to the distance d_{hkl} between planes and, neglecting other factors, the spot intensity should decrease continuously with the value of d_{hkl} corresponding to the plane. If, on the other hand, we have a cubic crystal made of two interpenetrating face-centered systems, (of which Fig. 9-14 represents a section through a (100) face), the situation is altered. If alternate atoms have a very different scattering power for X-rays, if for example the effect of the circles of Fig. 9-14 is negligible, it is readily seen that the planes with odd indices contain relatively more scattering centers than in the case of the simple cubic system (a simple cubic system would correspond to equality between the dots and circles of Fig. 9-14). Thus in a face-centered system in which one type of atom is a better scatterer than the other, the intensity of odd-order spots is enhanced. As the true scattering power of an atom is roughly pro-

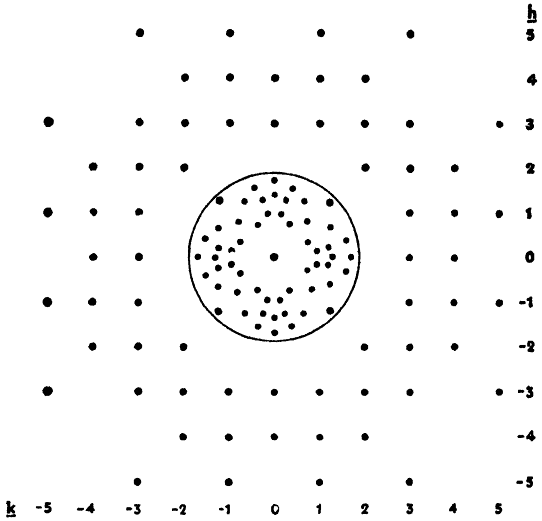

FIG. 9-13.—The gnomonic projection of a sodium chloride pattern. A sketch of the corresponding Laue pattern is shown in the center.

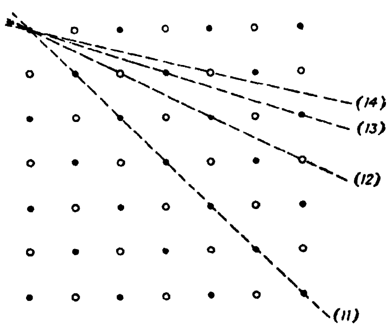

FIG. 9-14.—A section through a (100) plane of a system made up of two interpenetrating face-centered lattices.

portional to the number of extranuclear electrons it contains, *i.e.*, to its atomic number, we see that Cl($Z = 17$) is a better scatterer than Na($Z = 11$). In the case of sodium chloride the lattice points, which are occupied by ions, have 18 and 10 electrons associated with alternate points. Hence we should expect the enhancement of odd orders which is observed. In the case of potassium chloride ($Z = 19$ for potassium), each ionic lattice point has 18 electrons associated with it and the crystal should diffract X-rays in the manner of a simple cubic lattice.

Figure 9-15 is a reproduction of the Laue spot pattern obtained using a beam of X-rays normal to a cleavage face of calcite ($CaCO_3$). A similarity between this and Figs. 9-11 and 9-12 can be observed, but the pattern has not a fourfold symmetry about the normal through the central image. A gnomonic projection of such a picture yields spots which can be considered as lying on two sets of parallel lines which do not intersect at right angles or to rays of lines radiating from certain points. The proper assignment of index numbers, which with a knowledge of the values of unit crystal lengths determines the plane spacings and consequent wave lengths reflected, may be made by considering the intensities of the spots and the intensities of the various wave lengths present. From these data it can be shown that the correct unit crystal cell is not the one whose faces are parallel to the cleavage faces but is a rhombohedron with sides 6.36 Å long and apex angles of 46°6′.

9-6. Powder Method.—The principle of this method[1] has been discussed in detail in connection with the diffraction of electrons in Chap. V. A pencil of X-rays is incident upon a large number of small crystals oriented at random, and conical diffraction maxima coaxial with the direct beam are observed for those wave lengths and planes given by the Bragg expression [Eq. (9-3)]. The reason that the diffraction maxima are concentric conical shells is that all possible orientations of the small crystals about the X-ray beam are present; half the semiapex angle of a cone is equal to the Bragg angle θ for a plane. It is evident that if X-rays of all wave lengths are present there will be no preferred conical shells, for there will be a continuous range of θ corresponding to the continuous range of λ. If, however, certain wave lengths are much more intense than the background radiation, there will be a series of coaxial conical shells corresponding to the series of Bragg planes for each of these wave lengths. To reduce the number of these, monochromatic radiation is generally used for crystallographic work with this method.

The experimental arrangement used for the production of Laue spots, as shown in Fig. 9-7, can also be used to obtain powder photographs. If the method is to be used for making relative-intensity measurements for reflections from the various crystal planes, the recording arrangement should be a strip of X-ray film bent into the form of a cylinder whose axis passes through the crystal powder at C and is normal to the X-ray beam. This strip should extend for at least 90° on either side of its intersection with the direct beam; a radius of curvature of from 3 to 5 cm. is satisfactory for general purposes. As all points on the intersection of the plane containing the X-ray beam and normal to the axis of the cylinder are equidistant from the crystal powder, intensity measurements may easily be made, and furthermore the distances along the film, in this meridian plane, from the image of the direct beam to the intersections of the conical diffraction shells are directly proportional to the Bragg angles.

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[1] DEBYE and SHERRER, *Physik. Zeits.*, **17**, 277 (1916); **18**, 291 (1917). HULL, *Phys. Rev.*, **10**, 661 (1917); **17**, 571 (1921).

If, however, the relative intensities are not of particular importance the other information given by powder photographs can be obtained as well with a flat photographic plate as in the Laue spot arrangement. The intersections of the conical diffraction shells with this plane normal to their axes are circles, and the radii of these circles are given by Eq. (5-41)

$$r = \frac{S\lambda}{a}(H^2 + K^2 + L^2)^{\frac{1}{2}} \tag{9-8}$$

where S is the distance from the powder to the plate, a is the lattice constant of the cubic crystal, and H, K, and L are the plane indices. Thus from a measurement of the radii and S, and a knowledge of the wave length, it is possible to determine the type of crystal and the lattice constant a, at least in simple cases.

The most convenient method of obtaining monochromatic X-rays for this diffraction experiment is by the use of an appropriate filter. As will be seen later, zirconium, which is obtainable in sheets of oxide of uniform thickness, is a very convenient filter for radiation from a molybdenum target. The wave lengths $\lambda = 0.707$ and 0.712×10^{-8} cm. designated as K_{α_1}, K_{α_2}, are but little absorbed, whereas the intensities of the other characteristic wave lengths as well as the general white radiation are greatly reduced. The filter may be put over the first pinhole at A, or, if a large enough sheet is available, it may be placed between the crystal specimen and film or plate. The crystal powder itself may be mounted in a number of ways. A hole, about the size of that in C of Fig. 9-7, may be made in a sheet of celluloid a few tenths of a millimeter thick, the powder packed in it and the ends closed by cementing sheets of cellophane over them. Or the powder may be packed in a cellophane or thin-walled glass tube a millimeter or so in diameter and this tube mounted over the hole C, normal to the axis of the beam. If sheets of these randomly oriented crystal aggregates are available such as gold foil or leaf, these may be mounted directly over the diaphragm C, as is the single crystal for Laue photographs. For reasons which are obvious from the geometrical arrangement, the necessary exposure time is in general longer than for Laue pictures. For intense photographs, exposures of the order of 50 or 100 milliamp.-hr. are usually necessary.

Figure 9-16 is a reproduction of a photograph of gold foil about 1.5×10^{-3} cm. thick (32 thicknesses of standard gold leaf). The exposure was about 60 milliamp.-hr. The rings correspond to the intersection of the diffraction cones due to the MoK_α lines, with a plane film (Eastman nitrate ultra speed dupli-tized X-ray film) at a distance of 2.2 cm. Nine rings are visible in the original photographs, and, taking the value of the wave length of the X-rays as known, the lattice constant a of the face-centered gold structure is calculated, by the correct assignment of ring diameters and indices as in Chap. V, to be 4.05×10^{-8} cm. Alternatively if a were known, λ could be calculated. This value of a is in good agreement with that calculated from the density and checked by the electron-diffraction photographs of Chap. V. The similarity between the patterns of Figs. 9-16 and 5-13, one of which was obtained with X-rays and the two others with electrons, is very striking. The same crystal-lattice theory is used in interpreting both, but one is the result of the diffraction of electromagnetic waves while the other two are due to the diffraction of the phase waves associated with electrons.

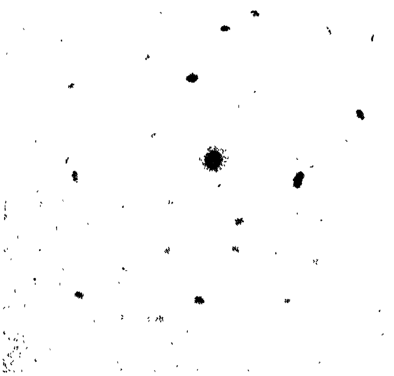

FIG. 9-15.—The Laue spots due to diffraction of a continuous wave-length range of X-rays by a calcite crystal (rhombohedral type).

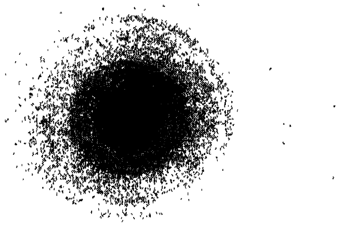

FIG. 9-16.—The X-ray diffraction rings formed by the molybdenum K_α lines on passing through randomly oriented gold crystals.

9-7. Rotating-crystal Method.—A third method of crystal or X-ray analysis, supplementary to the two which have been mentioned, and of the greatest practical importance, is the oscillating- or rotating-crystal method, due to Bragg.[1] In this method the crystal oscillates or rotates about an axis parallel to one of the crystal axes and perpendicular to the X-ray beam. From time to time certain of the crystal planes make the correct Bragg angle with the X-ray beam for certain wave lengths. As in the powder method the resulting pictures are simpler if monochromatic X-rays are used, but as the photographs are easier to interpret than those obtained with powder this is not essential. As can be seen from the geometry of the arrangement, if a photograph obtained by complete crystal rotation is rotated about the X-ray beam axis, the spots trace out the circles of the powder photographs. In taking oscillating-crystal pictures the crystal turns only through a limited angle and hence all the possible rotation spots do not appear. As will be seen in the discussion of a sample picture, this method yields a measure of the volume of the correct unit cell.

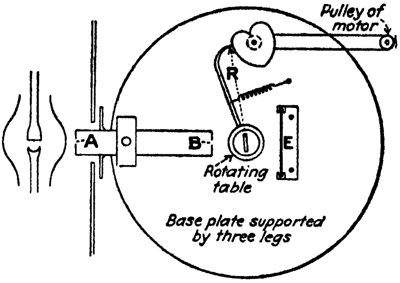

Fig. 9-17.—An experimental arrangement for the oscillating-crystal method.

For rough or preliminary crystal measurements the apparatus for obtaining Laue spots (Fig. 9-7), can be used with the cylinder supporting the pinholes in the same position. The diaphragm *C* is, however, removed and the crystal mounted on a rod extending up nearly to the X-ray beam from a small table capable of rotating about a normal to the beam. This table (see Fig. 9-20) rotates in a bearing which, on the suggested dimensions, is about 4 cm. from the pinhole *B*. The plate holder is placed an equal distance behind the crystal table. Figure 9-17 illustrates the experimental arrangement and the method of producing the crystal oscillations in such a way that the rotation is at a constant rate for a constant speed of the driving motor. The crystal table which sits in a brass bearing is rotated about a vertical axis by an arm held against the cam by a spring. The cam is turned through a pulley and worm reduction gear by a small direct-current electric motor whose speed can be controlled with a rheostat. The speed of rotation of the cam is not critical; for small angles of oscillation 10 or 15 r.p.m. is satisfactory. The proper shape of the cam may be determined as follows. If R is the length of the arm from the center of rotation to the point of contact with the cam, and r is the distance from the center of rotation of the cam to this variable point of contact, we have

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[1] Bragg, W. H. and W. L., *Proc. Roy. Soc.*, **88**, 428 (1913); **89**, 246, 248 (1914). Wyckoff, "The Structure of Crystals," Chap. V, Chemical Catalog Company (1931).

$$\frac{r - r_0}{R} \cong \phi \quad \text{or} \quad \frac{dr}{dt} = R\frac{d\phi}{dt}$$

where ϕ is the angular rotation of the crystal from the arbitrary zero chosen when the arm is at the bottom of the reentrant angle of the cam, and where the minimum radius of the cam is r_0 and the maximum is, say, r_1. If $d\phi/dt$ is to be constant then so must also dr/dt and since the rate of rotation of the cam, say $d\psi/dt$, is uniform, then $dr/d\psi$ must be constant. That is,

$$r = A\psi + C$$

is the equation of the periphery of the cam. Therefore if $\psi = 0$ when $r = r_0$, and if $\psi = \pi$ when $r = r_1$, we have

$$r = \frac{r_1 - r_0}{\pi}\psi + r_0$$

as the equation of half the periphery. The total angle of oscillation of the crystal is $(r_1 - r_0)/R$. It is convenient to have several cams with different values of $(r_1 - r_0)$ which have collars and set screws for mounting on the cam axis, which fits in a bearing in the base plate. Cams which give a total rotation of 40° to 50° are useful for the type of photograph which is to be described, while smaller ones are more convenient for examining smaller spectral regions as will be mentioned in a later section.

The cam is set so that the crystal table is halfway between its two extreme positions and the crystal specimen is mounted on the table so that the X-ray beam is normal to a cleavage face and the axis of rotation is parallel to one of the principal crystal axes. A crystal of the thickness used for obtaining Laue spots is satisfactory. The adjustment may be performed, for example in the case of rock salt, by placing one of the cleavage edges on the table and adjusting the crystal until the light from the filament of the X-ray tube (with no potential applied to it) reflected from the target through the diaphragms A and B, is reflected back to B by the crystal face. If this light is too weak, an arc light may be focused on B through a hole in a black-paper screen at E on the axis of the X-ray beam, and the crystal adjusted until, as it rotates, the beam reflected by it back to the screen traces a line through the hole, extending an equal distance on either side of it. The crystal is fastened to the table by a bit of soft wax or paraffin; in the latter case the paraffin is softened with a warm soldering iron for adjustment of tilt. For total rotation angles of about 45° exposures of the order of 10 to 20 milliamp.-hr. are in general sufficient.

Figure 9-18 is an oscillation photograph taken with the unfiltered radiation from a molybdenum target, using a crystal of sodium chloride rotated about one of its cubic axes. The horizontal line about which the picture is symmetrical is perpendicular to the beam and the axis of rotation. The crystal oscillated only through a large enough angle to give reflections from the (010) planes and the first reflection from the (021) plane along this line. In going out from the central spot along the meridian line the first darkening is due to the continuous radiation, the second to the K_β, and the third to the K_α lines reflected from the (010) planes. The next two spots occur at twice the angles of these and are the next-order reflections of these lines. The last spot is due to a different type of plane, *i.e.*, (021). The other prominent lines extending across the picture at 45° to the meridian line also correspond to spectral dispersions. Those spots almost directly above or below spots on the meridian line designated by $(0kl)$ are due to planes of the form $(\pm hkl)$ where h and k are approximately inversely proportional to the rectangular coordinates of a spot in the photograph. The horizontal lines of spots parallel to the meridian line are known as *layer lines*. If two adjacent similar atoms on the axis of rotation are considered, spots on the meridian line correspond to diffraction maxima of zero path difference between these atoms, whereas the first, second, etc., layer lines above and below, are due to diffraction patterns for which the path difference from these atoms is λ, 2λ, etc. Thus from a knowledge of the wave length, the crystal-lattice constant a may be calculated. Assuming that the darkest spots correspond to the first-order reflections of the molybdenum K_α lines, a measurement of Fig. 9-18 to obtain θ for Eq. (9-3) yields a value of a equal to 2.8×10^{-8} cm. In order to see if this is the correct unit-cell dimension we may calculate how many atoms of each kind it contains; this must come out integral. Taking the density as 2.17, the mass of a cell 2.8×10^{-8} cm. on a side is 4.76×10^{-23} gram. The mass of one atom of sodium is 3.79×10^{-23} gram and of one atom of chlorine is 5.85×10^{-23} gram or the mass of one sodium and one chlorine atom is 9.64×10^{-23} gram. Hence a cell 2.8×10^{-8} cm. on a side contains but half a sodium and half a chlorine atom. If, on the other hand, we had assumed that the darkest spots were second-order reflections, the first being absent or very faint, we should have obtained a unit cell 5.6×10^{-8} cm. on a side containing four sodium and four chlorine

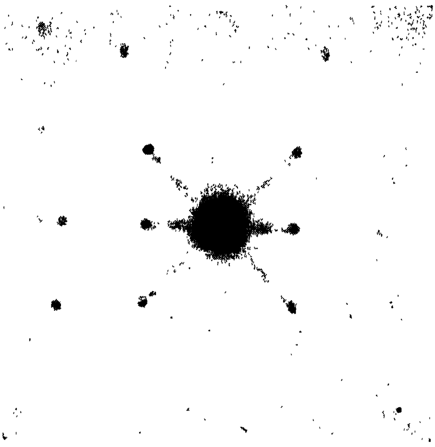

FIG. 9-18.—An oscillation photograph using unfiltered molybdenum radiation and a sodium chloride crystal.

atoms, so that this is the correct unit cell assignment. As we have seen from the Laue spot picture of sodium chloride, we may think of the crystal as a simple cubic crystal with sodium and chlorine ions placed at alternate lattice points, or as two interpenetrating face-centered sodium and chlorine lattices each with twice the grating space. With potassium chloride, where the simple cubic-lattice points are practically identical, there is no direct evidence of the interpenetrating face-centered system. But in the original photographs with sodium chloride a faint layer line appears halfway, between the first intense one and the meridian line, corresponding to twice the simple cubic-lattice constant. For this layer line two neighboring chlorine atoms contribute to the diffraction maxima, one wave length out of phase. The sodium atoms between are one-half wave length out of phase with the chlorine atoms, but as they are not as efficient scatterers the maxima are not completely obliterated.

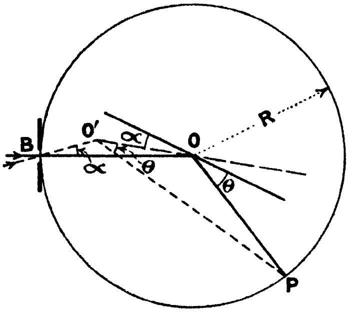

Fig. 9-19.—The focusing property of the rotating-crystal method.

For precision work in measuring lattice constants or wave lengths the preceding arrangement is not adequate. In order to measure these quantities accurately, the dispersion radius must be made larger and the detecting device, which may be either a photographic film or an ionization chamber, must lie upon a circle whose center is on the axis of rotation of the crystal and whose circumference contains the defining slit of the X-ray beam, *i.e.*, $OB = R$, the radius of curvature. When these conditions are fulfilled we see from Fig. 9-19 that we obtain a focusing effect and the images of the slit formed on a curved photographic film are very sharp. Let us assume that the crystal face rotating about O intercepts all of the rays in the divergent bundle leaving B. If the central ray of this bundle, passing through the center of rotation O, is reflected at the Bragg angle θ through the point P, it can be shown that any other ray making an angle α with the central one is also reflected through the point P, where $OP = OB = R$, when the crystal has rotated through an angle α. Thus, from Fig. 9-19, we see the following trigonometric relations from the triangles $BO'O$ and $PO'O$:

$$\frac{OO'}{\sin \alpha} = \frac{R}{\sin (\pi - \theta)}$$

and

$$\frac{OO'}{\sin [\pi - (\pi - \theta - \alpha) - \theta]} = \frac{OP}{\sin \theta}$$

Hence $OP = R$. As the crystal rotates, each ray of the divergent bundle is reflected from a different point on the crystal face to the point P if the crystal is perfect. The effect of the focusing condition is also to smooth out small imperfections in the crystal face. This method of "reflecting" X-rays from the cleavage face of a thick crystal has the further advantage that the diffraction maxima due to other crystal planes are not evident.

For photographic work the essential elements of Fig. 9-17 can be used, but the apparatus is moved farther away from the tube so that the cylinder supporting the diaphragms may be pushed through the collar away from the center of rotation of the crystal. Using the suggested dimensions, the distance from B to the axis of rotation may be made about 13 cm. (see Fig. 9-22). A and B are replaced by lead slits about 1 and 0.1 mm. in width, respectively. A may be made by a saw cut in a lead or lead-alloy sheet, the edges being smoothed with a small file. B is preferably an adjustable spectroscopic slit fitted with lead jaws, but it may be formed by two straight-edged lead strips mounted with soft wax over a coarse slit in a supporting plate and pressed together upon a shim or piece of heavy paper to obtain the correct separation. The film holder is a cylindrical metal frame with its center at O and its radius equal to OB of Fig. 9-19. This may be adjusted in position and screwed to the base plate. If it is not desired to photograph lines beyond 1.5 Å with rock salt (or second-order of the K_α lines of molybdenum on both sides of the zero), the cylindrical frame need not extend over more than about 45° on either side of the direct beam. The film may be held against the frame with clips or rubber bands.

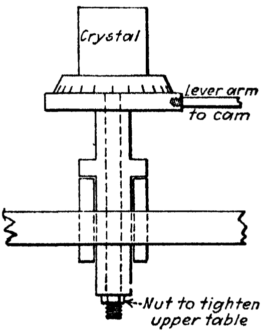

FIG. 9-20.—The details of a crystal mounting.

The crystal for use in this arrangement should have a broad enough face so that it intercepts all the X-rays leaving the slit B when set at the proper Bragg angle for reflection from this face. The height of the crystal in general determines the length of the spectral lines obtained. For the work to be described, a rock-salt crystal with the reflecting face 2 cm. square and a thickness of about 1 cm. may be used satisfactorily. The proper mounting of the crystal for precision work is difficult.[1] For work in which only moderate accuracy is desired, the following method is satisfactory. A No. 60 drill is mounted in a hole made on the axis of rotation of the crystal table and the cylinder supporting the slits is rotated until, by the light reflected from the target with the filament on, the slits are adjusted parallel to the drill. The plane defined by the beam then contains the axis of rotation of the table. The drill is removed and the crystal placed with one cleavage face flat on the table and held with its prepared perpendicular cleavage face over the center of the hole and against a small metal cube to assure that this face is normal to the table and contains the axis of rotation. It is then fastened in position by flowing paraffin along the edges in contact with the table.

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[1] SIEGBAHN, "Spectroscopy of X-rays," Oxford University Press (1925); "Spektroskopie der Röntgenstrahlen," Springer (1931).

WYCKOFF, "The Structure of Crystals," p. 167ff, Chemical Catalog Company (1931).

SCHLEEDE and SCHNEIDER, "Röntgenspektroskopie," deGruyter (1929).

NIGGLI, OTT, and HERTZFELD, *Handbuch der Expt. Physik*, vol. VII (1928).

With the table arm in contact with the cam at one extreme position, the table top is rotated until the crystal face is parallel to the X-ray beam, the crystal being on the proper side of the beam so that during the cam rotation the X-rays strike the prepared cleavage face. The table top is then clamped in position by means of the nut shown in Fig. 9-20. A film is then mounted on the cylindrical holder and the crystal set in oscillation. If it rotates through 18° or 20° on one side of the central beam, which is sufficient to obtain the second-order of the K_α lines of molybdenum, an exposure of about 15 milliamp.-hr. is sufficient. To obtain the orders on the other side, the crystal is set parallel to the beam and on the opposite side of it with the cam in its other extreme position and a similar exposure made. Figure 9-21 shows a typical photograph made with this arrangement. On the original film the four characteristic lines of the K series of molybdenum are visible in two orders on either side of the central image. Two dark edges are also visible on either side. These are due to the silver and bromine in the photographic emulsion. As we shall see later, there are certain critical wave lengths for absorption by each element. Shorter wave lengths, capable of exciting the characteristic radiation of the element, are strongly absorbed while longer ones are not. The absorption and consequent electron emission for these two elements in the emulsion are responsible for these dark edges. A measurement of the film on a comparator, together with a knowledge of the radius of curvature and the crystal-lattice constants, permits the calculation of the wave lengths of the lines and edges. The linear distance between two lines in similar orders divided by twice the order and the radius of curvature yields 2θ, from which λ can be calculated

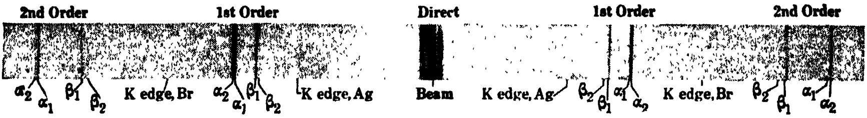

FIG. 9-21.—The X-ray spectrum from a molybdenum target obtained by reflection from a rotating sodium chloride crystal. The K absorption edges of the silver and bromine in the photographic film are indicated.

by means of Eq. (9-3). The weighted means of the measurements obtained from Fig. 9-21 are given below.

	λ (calculated)	λ (accepted)
First absorption edge (Ag)	485×10^{-11} cm.	484.48×10^{-11} cm.
First line (Mo, K_{β_2})	621	619.698
Second line (Mo, K_{β_1})	632	630.978 631.543
Third line (Mo, K_{α_1})	707	707.831
Fourth line (Mo, K_{α_2})	712	712.805
Second absorption edge (Br)	920	918.09

The significance of these emission lines and absorption edges will be discussed in a later section.

For quantitative intensity measurements the X-rays are detected by the ionization they produce in a chamber rather than by their effect on a photographic plate. Designs for precision ionization-spectrometers are given in the references[1] which have already been cited, but a simple adaptation of the type of apparatus which has been previously described is adequate for the measurements suggested in the following sections. A brass disk with a hole in the center which fits snugly the outside of the crystal-table bearing, rests flatly upon the base plate. The periphery

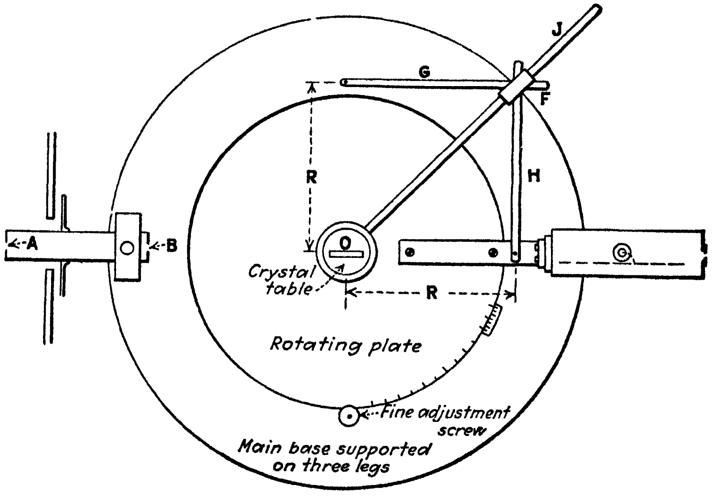

FIG. 9-22.—An experimental arrangement for the use of an ionization chamber in the analysis of x-radiation.

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[1] SIEGBAHN, "Spectroscopy of X-rays," Oxford University Press (1925); "Spektroskopie der Röntgenstrahlen," Springer (1931).

KIRCHNER and LINDH, *Handbuch der Expt. Physik*, vol. XXIV (1930).

is beveled and graduated for about 60°, and a vernier scale is provided on the base plate. A knurled knob in a small bearing tangent to the circumference of the disk carries an inverted rubber cone which engages the bevel by friction and permits of fine adjustments in the setting of the disk. An arm extending radially carries the ionization chamber on a bakelite block with its front slit at a distance equal to *BO* from the axis of rotation. Designs for ionization chambers are also given in the references, but a simple one can be made from a piece of brass tubing about 6 in. long and $1\frac{1}{2}$ in. in diameter. This is closed at either end with brass disks containing slots about 2 cm. long and 0.1 cm. wide, parallel to the slits at *A* and *B*. These slots are closed by cementing cellophane over them. The front one is of lead and may be of the same construction as slit *B*. It is supported by a short piece of 1-in. brass tube threaded into a collar on the front of the chamber. A bakelite or amber plug passing through the top of the chamber supports a brass rod parallel to the chamber axis but displaced out of the direct beam. If leakage difficulties across this plug are encountered, a grounded guard ring may be placed around the electrode through the plug; this may be a brass tube put through the plug and filled with sealing wax to support the electrode which runs coaxially through it. A stoppered hole is provided in the top of the chamber for admitting a few drops of methyl iodide or ethyl bromide. These heavy vapors have a large volume coefficient of absorption and greatly increase the efficiency of the ionization chamber. The chamber is maintained about 100 volts above or below ground, and the inner electrode is connected through a grounded metal tube to the electrometer or amplifying tube. For accurate work with weak X-ray beams the electrometer must be quite sensitive and a rate of deflection method used. In this case the leads must be of small capacity; a fine wire strung on quartz rods through 1-in. brass tubing to an electrometer mounted above the axis of rotation is the general practice. A swivel joint on this axis permits the rotation of the chamber and lead. For the measurement to be described, however, this refinement is unnecessary and a semiflexible lead-sheated rubber cable with a single copper wire down the center connects with an ordinary electrometer set up. With a sensitivity of 2,000 or 3,000 divisions per volt the constant-deflection method may be used.

The crystal rotation through half the angle of the ionization chamber is effected by the arrangement shown in Fig. 9-22. A brass rod *G*, having a pin in one end, which fits in the bearing previously used for the cam, is jointed at *F* to a similar brass rod *H*, whose other end is constrained to rotate about a point on the arm supporting the ionization chamber at a distance *R* from the center of rotation. The junction of these rods supports a brass sleeve, also free to rotate about the point *F*, through which a cylindrical brass rod *J* of length 2*R*, fastened at one end to the crystal table, is free to slide. From the geometrical arrangement it is seen that this rod rotates the crystal table through half the angle of the ionization chamber.

The chamber is first lined up with the direct beam by sighting through it over the center of rotation to the tube target as seen through the slit *B*. Then it is rotated through the calculated angle for observation of one of the strong characteristic lines in the first order. With the tube in operation the crystal table top is turned and small adjustments are also made in the ionization-chamber setting, until the electrometer current is a maximum. The crystal is then clamped in position. If the apparatus is ruggedly made, this adjustment should not require alteration over considerable periods of time. The use of this apparatus for determining the value of Planck's constant from the short wave-length limit and the tube voltage, and for making absorption measurements, will now be described.

9-8. Short Wave-length Limit and Planck's Constant.—We may consider the generation of X-rays by electrons bombarding a target as being very closely analogous to an inverse photoelectric effect; instead of electrons being liberated under the influence of radiation, X-rays are produced as a result of electron bombardment. The radiation emitted from an anticathode may be divided into two classes for purposes of discussion. There are certain very strong monochromatic beams whose wave lengths are characteristic of the element of the target, and in addition there is a continuous background of radiation known as the *continuous spectrum.* As in the case of black-body radiation, the mechanism of the emission of this continuous spectrum is not completely understood. In a qualitative way we may think of it as due to the stopping of the electrons at one or more collisions and the emission of the kinetic energy in a radiant form. The shortest wave length present will correspond to the complete loss of the kinetic energy of an electron in a single process, and by Einstein's equation $eV = h\nu$ (the work function $e\phi$ being negligible in comparison with eV), we see that this shortest wave length should be associated with the potential applied to the X-ray tube by the relation

$$\lambda_0 = \frac{c}{\nu_0} = \frac{ch}{eV_0}$$

or expressing λ_0 in Ångströms, V_0 in volts, and e in electrostatic units,

$$\lambda_0 V_0 = \frac{ch}{e} \times 300 \times 10^8$$

Thus from a knowledge of λ_0, V_0, c, and e, we may calculate the value of Planck's constant, h. This is one of the most accurate ways of obtaining this quantity, and as a final check on the theory the results agree very well with those of other methods. The following values of h are those which have been most recently found from the short-wave-length limit.

Wagner[1]	$(6.526 \pm 0.01) \times 10^{-27}$
Duane, Palmer, and Yeh[2]	(6.556 ± 0.009)
Feder[3]	(6.547 ± 0.003)

This experiment can be performed to an accuracy of about 2 or 3 per cent with the ionization spectrometer that has been described. The method is to set the potential across the X-ray tube at some known value as measured with a sphere gap, and plot the ionization current through the electrometer as a function of the angular setting of the chamber. As it is only necessary to determine the point at which intense ionization sets in, these angular displacements need not be continued much beyond the break in the resulting curve. Figure 9-23 represents a typical series of curves obtained at five different voltages with a generator using a mechanical rectifier and no capacity. Since the voltage fluctuates between zero and its maximum value, which is that measured by the sphere gap, the break in the curve corresponds to the shortest wave length emitted by those electrons which have fallen through the peak voltage. The breaks are sharper if a constant-potential source is used. The ionization currents on the small-angle side of the breaks do not have

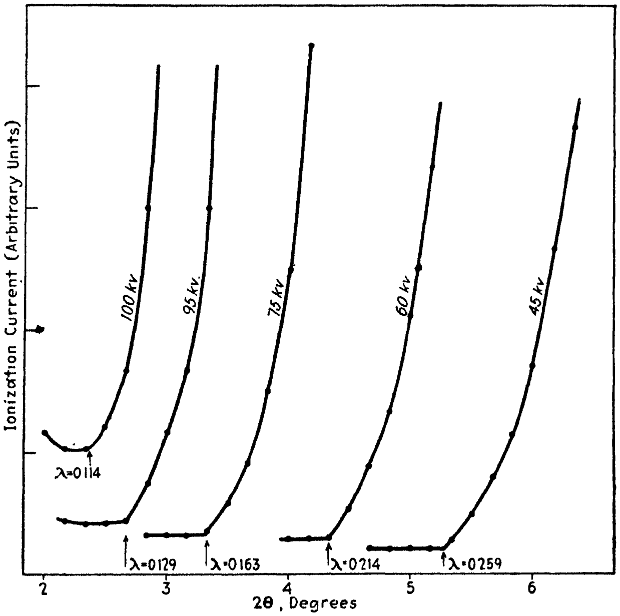

FIG. 9-23.—The variation of the short-wave-length limit of the X-ray spectrum with the applied potential as determined with an ionization chamber and crystal spectrometer.

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[1] WAGNER, *Physik. Zeits.*, **21**, 621 (1920).

[2] DUANE, PALMER, and YEH, *Proc. Nat. Acad. Sci.*, **7**, 237 (1921).

[3] FEDER, *Ann. Physik*, **1**, 497 (1929).

a common zero and they rise very sharply at values of 2θ less than 2° due to the spreading of the direct beam and to X-rays which are scattered irregularly at small angles from the crystal face. On the basis of these five peak voltages and angular settings (2θ), we obtain the average value 12,070 for the product $\lambda_0 V_0$. Taking $c = 3 \times 10^{10}$ and $e = 4.77 \times 10^{-10}$, we find that $h = 6.39 \times 10^{-27}$, which is in error by about 2.5 per cent, approximately the accuracy of the sphere-gap measurement. This is less accurate than the determination from the photoelectric experiment, but it provides an adequate check on our conception of the process of X-ray emission.

9-9. X-ray Absorption.—Though almost all substances are much more transparent to X-rays than to visible light, an appreciable amount of energy is lost from an X-ray beam when it traverses a sheet of matter. If the amount of energy abstracted from a beam per unit length is proportional to the intensity of the beam, the decrease in intensity in traveling a distance dx may be written

$$dI = -\mu I dx$$

where μ is a constant of proportionality known as the absorption coefficient per unit length, and I is the intensity. This equation may be integrated directly, and the constant introduced may be determined by the condition that when $x = 0$, $I = I_0$. We then have

$$\begin{aligned} \log I &= -\mu x + \log I_0 \\ I &= I_0 e^{-\mu x} \end{aligned} \tag{9-9}$$

If a narrow beam of homogeneous X-rays is sent through varying thicknesses of matter this law is found to hold very well, hence under these circumstances we may consider that our assumptions leading to the exponential law are correct. If we compare the absorption of a broad beam of X-rays with that of a narrow one, we find that the broad beam is apparently not so greatly absorbed. This is what we should expect if there are two mechanisms of absorption: first, a true photoelectric or fluorescent absorption which corresponds to a transference of radiant energy into energy of excitation and kinetic energy of an electron; and, second, a scattering of the electromagnetic radiation through large enough angles so that it is lost to the beam. The second process would obviously depend on the beam width, for this type of scattering through small angles would not remove energy from a wide beam whereas it would from a narrow one. As a consequence we may consider the absorption coefficient μ to be made up of two parts, one the true photoelectric absorption coefficient τ, and the other the scattering coefficient σ.

$$\mu = \tau + \sigma$$

In general σ is very much smaller than τ.

While this separation of μ into two coefficients, one representing the so-called true absorption and the other simply the change in direction of the radiation, is a convenient method of attack on the problem, it must be remembered that this unduly simplifies the complicated phenomena concerned in the removal of radiation from a beam. We may obtain a further insight into the detailed processes by considering the application of the ideas discussed in the last chapter to radiation of X-ray wave length. A photon may be scattered elastically or it may be scattered inelastically with the production of an excited or ionized atom. After the loss of this energy, the photon's wave length is increased and its direction of propagation is changed (Compton effect). The atom may then return to its normal state by the emission of the radiation characteristic of the necessary readjustment; this depends on the energy state of the particular electron removed, as well as on the type of the absorbing atom. The original scattered and the secondary radiation then repeat these processes in passing through the matter; the wave length becomes increasingly longer and the direction of propagation is eventually quite at random. In addition to the primary and secondary radiation, the ejected electrons, which may possess large energies, are also capable of exciting other atoms on impact with a resulting tertiary type of radiation. The primary processes all correspond to a loss of energy from the original beam, and all the contributions from the random scattered, secondary, and tertiary radiations are so small that to a first approximation they may be neglected.

The linear absorption coefficient μ may be considered to be a measure of the energy abstracted from an X-ray beam by all processes in traversing a unit length of the absorbing substance. If the unit of length is the centimeter, $1-e^{-\mu}$ is the fraction of the energy absorbed per cubic centimeter from a beam of 1 square centimeter in cross section. It is more convenient to deal with the absorption coefficient per gram known as the mass absorption coefficient

$$\mu_m = \frac{\mu}{\rho}$$

where ρ is the density, or with the absorption coefficient per atom in the path of the beam,

$$\mu_a = m\mu_m$$

where m is the mass of an atom. Since $m = M/N$, where M is the atomic weight and N is Avogadro's number, we have

$$\mu_a = \frac{\mu M}{\rho N}$$

This quantity obviously is a direct measure of the ability of an atom to absorb or divert energy from the beam of X-rays. It is found that it depends both on the particular type of atom and on the frequency or wave length of the impinging radiation.

We find, if we measure the absorption coefficient of an element over a range of wave lengths, that μ_a increases about proportionally to λ^3 over a certain range and then drops very sharply at some value of λ. After this sudden decrease a second steady increase proportional to λ^3 again sets in, followed by a second sharp falling off, etc. The curve of μ_a against λ resembles the heavy line of Fig. 9-25 which shows one of these characteristic discontinuities. This type of absorption-coefficient curve is common to all elements, but the actual amount of absorption and the critical wave lengths differ from one element to another. It has been found empirically that the true absorption may be represented approximately over the region from very short wave lengths to the first discontinuity by the expression

$$\mu_a - \sigma_a = \tau_a = K'Z^4\lambda^3 \tag{9-10}$$

where Z is the atomic number of the scattering element and K' is a constant. A similar expression holds between successive discontinuities. This expression is generally known as Owen's law[1] and has been well verified by many investigators, most recently in the long-wave-length region by Jönsson.[2] This dependence of μ on λ is of great historical importance, for it was through the investigation of the absorption coefficients for a heterogeneous beam of X-rays that the presence of various characteristic wave lengths was first deduced by Barkla.[3] He designated the most penetrating radiation by the letter K, the next by L, etc. These terms are still current in X-ray nomenclature.

The characteristic discontinuities met with in proceeding to longer wave lengths bear a qualitative resemblance from one element to the next. The first discontinuity, which is a single one, is characterized by the letter K in accordance with Barkla's usage; then occurs a group of three, fairly close together, known as the L group; and these are followed by the M group which is composed of five members. It is found that the wave lengths at which these groups occur for different elements are inversely proportional to the square of the atomic number. The interpretation of these absorption limits and their connection with the characteristic X-ray line spectra of the elements will be dealt with in the following section. We shall first consider the verification of the exponential absorption law [Eq. (9-9)] and Owen's law [Eq. (9-10)].

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[1] Owen, *Proc. Roy. Soc.*, **86**, 426 (1912); **94**, 339, 510 (1918).
Bragg and Pierce, *Phil. Mag.*, **28**, 626 (1914).

[2] Jönsson, Dissertation, Uppsala (1928).

[3] Barkla and Sadler, *Phil. Mag.*, **16**, 550 (1908).

9-10. Experiments on X-ray Absorption.—Absorption measurements using a narrow beam of monochromatic radiation are readily made with an ionization spectrometer. The current through the ionization chamber, as measured by the electrometer deflection, is proportional to the intensity of the X-ray beam throughout the ordinary wave-length range. The crystal and chamber are set so that some wave length λ is being received, and the electrometer readings are noted as successive sheets of the absorbing substance are interposed between the crystal and the ionization chamber. For light substances, sheets about 10 mils (10×10^{-3} in.) thick are convenient, while for heavier substances they should not be thicker than 2 or 3 mils. The most accurate method of determining the thickness is to weigh a large sheet and divide its mass by the area times the density. These sheets should be as uniform as possible, both to obtain a correct measure of the thickness and an accurate value of the absorption coefficient. Eight or ten of the sheets $\frac{1}{2}$ in. wide and $1\frac{1}{2}$ in. long are sufficient. If their upper edges are bent into small hooks they may be suspended from a wire frame resting on the base plate of the spectrometer.

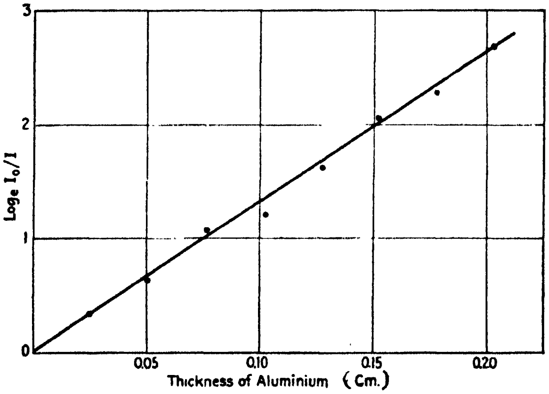

FIG. 9-24.—The absorption of the molybdenum $K\alpha$ lines by successive thicknesses of aluminium, as found with an ionization crystal spectrometer.

Figure 9-24 represents a plot of the $\log_e$ of the ratio of the ionization current with no screen to that with successive 10-mil aluminium sheets as a function of the thickness of the absorbing aluminium. The chamber was set to receive the K_α lines of molybdenum ($\lambda \cong 0.71 \times 10^{-8}$ cm.). It is seen that the points lie on a straight line in agreement with Eq. (9-9) and from the slope of this line the value of μ is found to be 13.2 cm.$^{-1}$. Dividing this by the density (2.7) we have $\mu_m = 4.89$ gram^{-1}, and multiplying this by M/N we obtain $\mu_a = 2.18 \times 10^{-22}$ per atom. The following table represents the absorption coefficient of Al, Cu, Ag, and Pt obtained with this type of apparatus using three different wave lengths. The ones chosen were: Mo K_α ($\lambda = 0.71 \times 10^{-8}$), Mo K_β ($\lambda = 0.63 \times 10^{-8}$), and a region where the continuous spectrum was quite intense at $\lambda = 0.5 \times 10^{-8}$ cm. The entries in the column μ_a/λ^3 should be constant for any particular element according to Owen's law. (No absorption discontinuities lie in this wave-length range for these elements.) The departure from constancy represents about the limit of error of the experiment. The column μ_a/λ^3Z^4 should be constant for all elements if the wave-length range lay between the same two critical absorption values for them. The range is below the K limit for Al and Cu but between the K and L limits for Ag and Pt. Hence the values for Al and Cu should be the same, as should those for Ag and Pt; this is seen to be the case well within the limits of error. As may be seen from the values in this last column the constant $K'_{\lambda<\lambda_K}$ is much greater than $K'_{\lambda_K<\lambda<\lambda_L}$ corresponding to a greater atomic absorbing efficiency for this region.

Absorption Coefficients

Element	$\lambda \times 10^8$ cm.	μ	μ_m	$\mu_a \times 10^{22}$	$(K'Z^4 = \mu_a/\lambda^3) \times 10^{-2}$		$(K' = \mu_a/\lambda^3Z^4) \times 10^2$	
							$\lambda < \lambda_K$	$\lambda_K < \lambda < \lambda_L$
Al								
ρ = 2.7	0.50	4.6	1.7	0.76	6.08	6.18	2.17	
M = 27	0.63	9.7	3.6	1.60	6.38			
Z = 13	0.71	13.2	4.9	2.18	6.09			
Cu								
ρ = 8.9	0.50	177	20	20.9	167	156	2.21	
M = 63.5	0.63	321	36	37.7	150			
Z = 29	0.71	463	52	54.4	152			
Ag								
ρ = 10.5	0.50	105	10	17.8	142	141	....	0.289
M = 108	0.63	210	20	35.6	141			
Z = 47	0.71	294	28	49.9	140			
Pt								
ρ = 21.4	0.50	1,070	50	161	1,290	1,120	....	0.295
M = 195	0.63	1,800	84	270	1,070			
Z = 78	0.71	2,400	112	360	1,000			

The shape of an absorption curve over a range of wave lengths may be found by measuring the ionization current through the chamber at a series of angular settings, both with and without an absorbing screen in place. From the ratio I_0/I and the thickness of the screen, μ, μ_m, and μ_a may be calculated. A very convenient screen with which to observe a critical absorption discontinuity is the ZrO_2 screen used for obtaining approximately monochromatic radiation from a molybdenum target.

The reason that the screen is effective for this purpose is that the absorption drops from a very high to a low value between the two strong characteristic lines K_β and K_α. The K_β line and shorter wave lengths are strongly absorbed whereas K_α is only reduced in intensity by a factor of about 2 by the standard ZrO_2 screen which is about 0.4 mm. thick. Figure 9-25 represents a run taken in this manner with such a screen. The ordinates of the dotted curves are proportional to the electrometer currents with and without the screen. These show the continuous radiation beginning at about 0.36 Å and the two K_β and K_α peaks. The heavy line is the ratio of these curves and its ordinates are equal to $I_0/I = e^{\mu x}$. The absorption by the oxygen is negligible, as its critical value is at much longer wave lengths, so this curve may be taken as a measure of the absorption of zirconium. It is seen that the absorption drops very rapidly between $\lambda = 0.67$ and 0.70 Å. We may take the wave length at which this sharp decrease occurs as 0.685 Å. It is the first break to occur as we proceed from short to long wave lengths and hence it is the K absorption limit of zirconium.

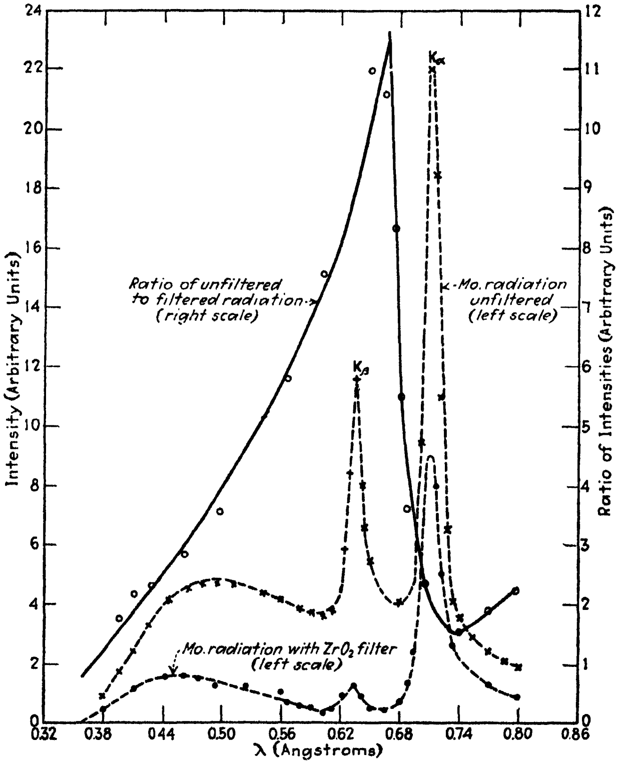

FIG. 9-25.—The absorption of zirconium in the region of a critical absorption edge.

If quantitative intensity measurements are not desired it is easier to obtain the values of the absorption limits photographically. The rotating-crystal method is used, and a layer of the absorbing substance is placed over the photographic plate or film. If a long slit is used, the absorption limits of several substances can be obtained at the same time. Several lengths of solder wire are waxed on a thin aluminium sheet 2 or 3 mm. apart. The troughs between the strips of solder are filled in with the substances whose absorption edges are to be photographed. A convenient method is to dissolve or suspend the substance or its oxide, nitrate, or carbonate in melted paraffin and pour this into a trough up to the level of the sides formed by the wires. The exposures need not be much longer than are required to obtain an intense photograph without the absorbing screens.

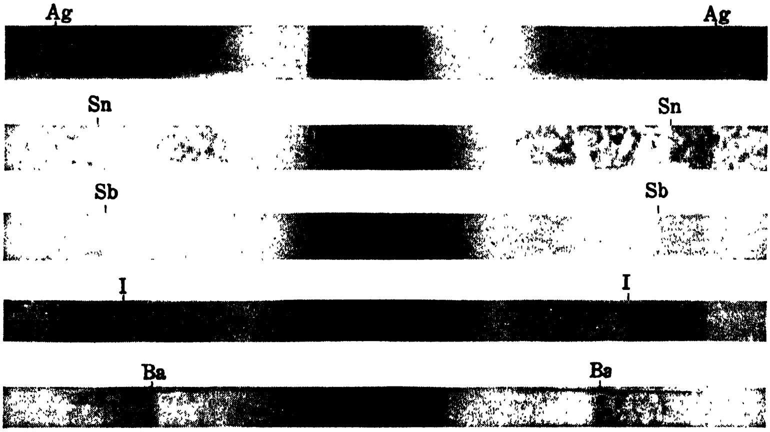

FIG. 9-26.—The *K* absorption edges of tin, antimony, iodine and barium, obtained with the continuous radiation from a molybdenum target. The *K* absorption edge of the silver in the film is visible in each spectrum.

Figure 9-26 represents a photograph taken by this method using paraffin suspensions of tin, antimony, iodine, and barium. No filter covered the plate for the top picture and the sudden decrease in darkening due to the change in absorption of the silver in the emulsion is alone evident. The succeeding pictures show abrupt increases of darkening at various shorter wave lengths. At these critical values the absorption of the material in front of the plate decreases sharply permitting the radiation of longer wave length to pass and affect the film. These absorption limits or edges are analogous to that of zirconium which was observed by the ionization method. The critical values of the wave lengths at which these absorption limits occur, as measured from Figs. 9-21, 9-25 and 9-26, are given in the table on page 362. The significance of this table will be discussed in the following section.

TYPICAL ABSORPTION DATA

Z	Element	λ_K (critical K absorption limit)	Accepted values
35	Br	0.925 Å	0.91809
40	Zr	0.685	0.68738
47	Ag	0.485	0.48448
50	Sn	0.425	0.42394
51	Sb	0.405	0.40609
53	I	0.375	0.37344
56	Ba	0.330	0.33070

9-11. X-ray Spectra and Atomic Structure.—We may now consider the interpretation of these absorption limits and the characteristic line spectra which have been observed. From the energies corresponding to X-ray frequencies we realize that in this region we must be dealing with electrons which are very closely bound to the nucleus. These are the inner electrons of low total quantum number which we have seen can be neglected in the explanation of ordinary optical spectra. The absorption limits bear a very close resemblance to the critical photo-ionization wave lengths which occur at the optical series limits. If the same type of interpretation is correct for this phenomenon, the frequencies corresponding to these absorption limits, when multiplied by h, must represent the energies necessary to remove an inner electron from an atom. The absorption limits observed in the preceding section are all those which occur at the shortest wave length for the particular substance. Hence these must represent the removal of an electron from the innermost energy level. By analogy with the optical discussion this would be the level in the particular atom for which the total quantum number n is equal to 1. In X-ray nomenclature this innermost level is known as the K level, since the removal of an electron from it corresponds to the K absorption limit. When absorption measurements are made at longer wave lengths, the other groups of absorption limits known as L and M are observed. They represent the removal of an electron from the group of levels characterized by total quantum numbers of $n = 2$ and 3, respectively. Still higher absorption limits which would be known as $N(n = 4)$, $O(n = 5)$, etc., should exist for heavy atoms. The M absorption limits for even uranium, in which these electrons are the most closely bound, are in the neighborhood of 3 Å, so that the subsequent limits for lighter elements would be well out of what is generally known as the X-ray region.

Since these absorption limits give us directly the ionization potentials or series limits, which represent the energy of the level as measured from the ion, we should expect upon the basis of the previous atomic theory that the difference between two of these levels in an atom would correspond to the energy of an emission line. This is in direct analogy with the previous discussion of optical spectra. It is actually found by experiment that the differences between these limits do correspond to emission lines, and on this evidence we may take over with great confidence the principles used in describing the radiation emitted by the outer electrons of an atom. There are, however, certain important differences. In X-ray excitation the outer electron is not raised to one of the possible higher unoccupied levels, but an inner electron, originally in a closed shell, is completely removed from an atom. The subsequent readjustment of the atom to the normal state may take place in several ways. If an electron is removed from the K level, one from the L level may replace it, and the vacancy so formed may be filled by an electron from the M level, and so forth, in a cascade process. On the other hand, the original unoccupied K level may be filled directly from the M or N or an outer level. Before the process of readjustment can be considered complete, an electron must be captured by the ion to replace the original one which was removed. All these different possibilities for transition, which are consistent with the ordinary selection rules of Chap. VII, are known to occur from the groups of lines which are emitted. By an extension of the optical equivalence of a shell containing one electron and a shell lacking completion by just one electron, we may be led to expect that the X-ray spectra of all elements, resulting as they do from the removal of an inner electron, will bear some resemblance to an ordinary one-electron or doublet spectrum. However, the similarity to be anticipated between the atomic hydrogen and an X-ray spectrum is realized only to a very rough approximation. The electric fields due to the nucleus and the other closely bound electrons are very intense, which greatly alters the simple theory holding when only one electron is involved. Also application of the Bohr orbital considerations leads to very high velocities for these inner electrons, which implies a large relativity correction on their mass.

As a first approximation, an explanation of X-ray spectra might be attempted by the extension of the simple Bohr theory indicated in Chap. VII. The wave number of the radiation emitted by an atomic system composed of a nucleus of charge Ze with one orbital electron would be given by the expression

$$\tilde{\nu} = RZ^2\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$$

where $R = 2\pi^2\mu e^4/ch^3$, and n and n' are the quantum numbers of the initial and final states respectively. It was actually found by Moseley[1] that the analogous X-ray lines of different elements may be represented very well by an expression of the form

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[1] MOSELEY, *Phil. Mag.*, **26**, 1024 (1913); **27**, 703 (1914).

$$\tilde{\nu}^{\frac{1}{2}} = K(Z - s)$$

where K and s are constants. Thus $\tilde{\nu}$ is found to be proportional to $(Z - s)^2$ rather than to Z^2 as the simplest theory would predict. For the K series s is approximately 1, and the various lines in the series can be represented if the constant K takes the values

$$K = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$$

where $n = 2$ for the longest wave-length line, $n = 3$ for the next, etc. Thus the approximate empirical form of the expression representing the K series is

$$\tilde{\nu} = R(Z - 1)^2\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$$

where $n = 2, 3, 4$, etc. This resembles very closely the Balmer expression. The quantity $(Z - 1)$ may be considered as the effective nuclear charge. It is $(Z - 1)$ instead of Z because of the screening effect, largely due to the other electron in the K level. The product $R(Z - 1)^2$ $(1/1^2)$ is the wave number of the K absorption limit, and hence is the value of the K X-ray term expressed in wave numbers. The other X-ray terms may be similarly expressed as

$$\tilde{\nu} = R\frac{(Z - s_n)^2}{n^2} \tag{9-11}$$

where $n = 2$ for the L levels, $n = 3$ for the M levels, etc. The quantity s_n varies with n and also with the atomic number. It ranges from about 8 to 22 for the L levels of different elements, from 15 to 44 for the M levels and from 27 to 64 for the N levels. This increase with atomic number and total quantum number agrees with the conception of it as representing the screening effect of other electrons in the atom.

We still have not considered the influence which the relativistic change in mass would have on these term values, nor have we taken into account the doubleness inherent in a one-electron hydrogen-like spectrum due to the two possible orientations of the electron spin vector. The first of these was treated by Sommerfeld[1] who showed that it was adequate to account for the observed multiplicity of the X-ray levels. Due to the introduction of the concept of electron spin into the theory of spectra, which occurred at a later date, the original treatment must be modified. The application of quantum mechanical methods to the subject by Heisenberg and Jordan[2] has led to the following complete expression for an X-ray term:

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[1] SOMMERFELD, "Atombau und Spektrallinien," 5th ed., Vieweg, Braunschweig (1931).

[2] HEISENBERG and JORDAN, *Zeits. Physik*, **37**, 263 (1926).

$$\bar{\nu} = R\left[\frac{(Z - s_{nl})^2}{n^2} + \alpha^2\frac{(Z - d_{nlj})^4}{n^3}\left(\frac{1}{l+\frac{1}{2}} - \frac{3}{4n}\right) + \alpha^2\frac{(Z - d'_{nlj})^4}{n^3}\,\frac{j(j+1) - l(l+1) - s(s+1)}{2l(l+\frac{1}{2})(l+1)}\right] \qquad (9\text{-}12)$$

The constants s_{nl}, d_{nlj}, and d'_{nlj} depend on the values of the subscripts, which all have the same significance as in ordinary optical spectra. The second term is the relativistic correction and the third is due to the orientation of the electron spin. The constant α, which is equal to $2\pi e^2/hc = 7.284 \times 10^{-3}$, is known as the fine-structure constant. We shall consider briefly the characteristics of X-ray levels and spectra on the basis of this expression.

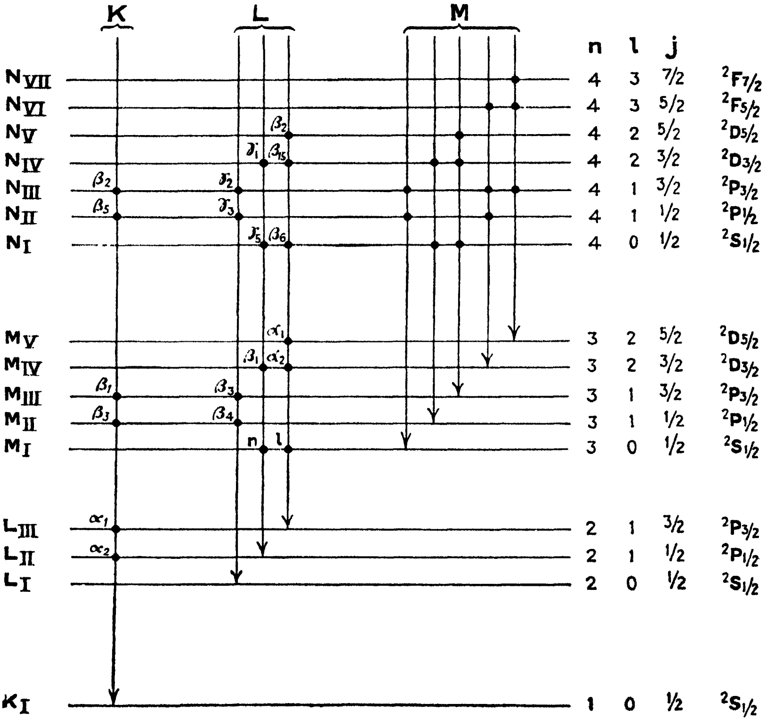

FIG. 9-27.—Typical X-ray levels and transitions. At the left is given the X-ray level nomenclature; on the right appear the quantum numbers of the electron that has been removed and the optical designation of the resulting term. Permitted transitions occur between dots and the heads of the vertical arrows. Siegbahn's notation for the lines is shown for the K and L series.

The levels predicted may be conveniently represented in a diagrammatic form as in Fig. 9-27. This is essentially similar to the Grotrian type of diagram. The actual values of these energy levels depend on the atomic number and characteristic constants of the element in question, but the general form of the scheme of levels is determined by the quantum numbers n, l, and j where $j = l \pm \frac{1}{2}$, since they are equivalent to a one-electron spectrum for which $S = \frac{1}{2}$. The lowest level for which $n = 1$ can only have $l = 0$ and hence $j = \frac{1}{2}$. The next set for which $n = 2$ is comprised of three, for two of which $l = 1$ with j values of $\frac{1}{2}$ and $\frac{3}{2}$ and one for which $l = 0$ with the j value of $\frac{1}{2}$. The values of n, l, and j are listed opposite the levels, the optical and X-ray terminology being given on the right and left, respectively. (As in all one-electron spectra, $s = S$, $l = L$, $j = J$.) The ordinary optical exclusion principles, $\Delta L = \pm 1$ and $\Delta J = \pm 1, 0$, determine the transitions to be expected. These are indicated by the vertical arrows, the predicted lines being transitions from the heavy dots to the termination of the arrow. The X-ray line nomenclature (Siegbahn) is indicated next to the dots, the characteristic symbol for a line series being given at the top of a column. These lines may equally well be referred to as in spectroscopic work by giving the initial and final level, *i.e.*, $K\alpha_2 = K_{\mathrm{I}} - L_{\mathrm{II}}$, $L\beta_3 = L_{\mathrm{I}} - M_{\mathrm{III}}$, etc.

As an example of the absolute magnitudes of the X-ray levels of a substance we may consider molybdenum, the K series of which are shown in Fig. 9-21.

The K absorption limit occurs at $\lambda_K = 0.61848$ Å which corresponds to a wave number of $1473.4 \times R$. The $\tilde{\nu}$ values of the other L, M, and N levels, for which transitions occur to the K level, may be found by subtracting the $\tilde{\nu}$ for the appropriate lines from that of the K limit. Alternatively values of $\tilde{\nu}$, for the L levels at least, can be found from direct-absorption measurements. The wave numbers of these levels measured from the ion and the combination lines which have been observed for molybdenum are given below in units of the Rydberg constant R.

Term	K_{I} 1,473.4	L_{I} 211.3	L_{II} 193.7	L_{III} 186.0	M_{I} 37.5	M_{II} 30.5	M_{III} 29.2	M_{IV} 17.3	M_{V} 17.1	N_{I} 5.1	$N_{\mathrm{II+III}}$ 2.9	N_{V} 0.4
K_{I} 1,473.4	....	.....	1,279.7	1,287.4	.....	1,442.9	1,444.2	.....	.....	.....	1,470.5	
L_{I} 211.3	....	.....	....	....	.....	180.8	182.1	.....	.....	.....	208.4	
L_{II} 193.7	....	.....	....	....	156.2	....	....	176.4	.....	188.6		
L_{III} 186.0	....	.....	....	....	.....	....	....	168.7	168.9	.....	....	185.6

When the wave numbers of these levels are translated into volts we see that the ionization potential from the level N_{V} is about 5.4 volts, while at the other extreme it requires about 20,000 volts to remove an electron from the K_{I} shell and excite the characteristic K lines. The L series should appear at an exciting potential of about 2,870 volts. From the wave number of the N_{V} level we see that we might expect photoionization from this level with light of wave length equal to 2270 Å; this is in the ordinary ultra-violet region.

We may now consider the application of Eq. (9-12) to the K-absorption limit data and the doublet separations of the K lines of molybdenum. If we neglect the effect of the second term, since α^2 is of the order of 10^{-5} (the third term is strictly zero for the K level since as $l = 0$, then $j = s$), we are left with Eq. (9-11) and, as $s_n = 1$ and $n = 1$ for the K level

$$\sqrt{\frac{\bar{\nu}}{R}} = Z - 1$$

Therefore a plot of the values of $\sqrt{\bar{\nu}/R}$ for the K absorption limits, which were observed in the preceding experiments, against Z should yield a straight line of slope and intercept equal to unity. How well this

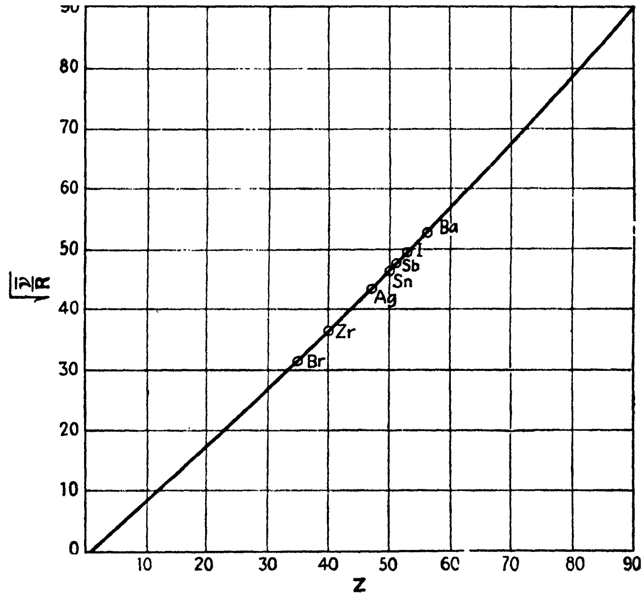

FIG. 9-28.—The variation with atomic number of the function $\sqrt{\bar{\nu}/R}$ for the K absorption limits.

is obeyed is seen from Fig. 9-28. The experimental points indicated by circles lie very well on a straight line with unit slope but with an intercept of $Z = 4$. The curve which extends through the other K limits, which have been observed from magnesium to uranium, is seen not to be strictly a straight line due to the higher order term of Eq. (9-12), but the extrapolation of the curve from points of low atomic number where this term has least effect indicates an intercept of $Z = 1$.

A further point of interest is in connection with the observed wavelength difference between the $K\alpha_1$ and $K\alpha_2$ lines of molybdenum, as measured from Fig. 9-21. This corresponds to a wave-number difference of approximately $7.7 \times R$, or from the most accurate measurements, 848,100 cm.$^{-1}$ or an energy difference of about 105 volts. From Eq.

(9-12) we see that the wave-number difference between two levels in an atom for which the n and l values are the same, (neglecting the difference between d and d' which is small) is given by

$$\tilde{\nu}_2 - \tilde{\nu}_1 = \Delta\tilde{\nu} = \frac{R\alpha^2(Z - d_{nl_l})^4}{n^3}\left[\frac{j_2(j_2 + 1) - j_1(j_1 + 1)}{2l(l + \frac{1}{2})(l + 1)}\right]$$

For the L_{III} level, $j = \frac{3}{2}$ and $l = 1$; for L_{II}, $j = \frac{1}{2}$ and $l = 1$; hence for this separation we have

$$\Delta\tilde{\nu} = \frac{R\alpha^2(Z - d)^4}{16}$$

or the fourth root of $\Delta\tilde{\nu}$ should be proportional to Z. As we saw in our discussion of the atomic hydrogen spectrum, the terminal level for the Balmer series, which corresponds to the L X-ray level, would be considered on the vector model to be made up of the three levels $^2P_{\frac{1}{2}}$, $^2P_{\frac{3}{2}}$, $^2S_{\frac{1}{2}}$, which have practically coalesced. From the above relation and the K_α doublet of molybdenum, we can calculate approximately the separation of the two P levels to be expected in the case of hydrogen. Taking the appropriate value of d, determined from other data as being about 3.5, we have

$$\Delta\tilde{\nu}_{\text{H}} = \frac{\Delta\tilde{\nu}_{\text{Mo}}}{(38.5)^4} = 0.3\ \text{cm.}^{-1}$$

for the separation of these hydrogen levels. This is in excellent agreement with the observed fine structure of the lines of the Balmer series.

CHAPTER X

RADIOACTIVITY

10-1. Introduction.—The study of the structure of matter entered a new phase with the discovery of radioactivity. This phenomenon consists in the spontaneous disintegration of certain of the elements resulting in their transmutation. From the fact that this property is entirely independent of chemical combination and of any external physical conditions, it is apparent that the mechanism of the breakdown is concerned with the nucleus of the atom rather than with the orbital electrons, whose number and arrangement constitute the chemical properties and which are susceptible to external forces. Although the behavior of the orbital electrons permits a certain amount of reasonable speculation as to the properties of the nucleus, and while the mass spectrograph allows its total mass to be obtained, radioactivity has given, for the first time, any positive data on its constituent parts and on the energy associated with them. The experimental technique is on the whole quite different from that of other branches of physics, due largely to the fact that excessively minute quantities of matter are handled, the effects of but a single atom often being observed, a fact which would have seemed utterly impossible a few score years ago. Although great progress has been made in this new field, since its discovery in 1896, the subject is far from being completely understood.

The initial discovery of radioactivity was made by Becquerel[1] in 1896, shortly after the first production of Röntgen rays. The fluorescence of the glass walls of an X-ray tube suggested that substances which fluoresced after exposure to visible light might perhaps also emit a penetrating radiation. While looking for this effect with a sulphate of uranium, Becquerel observed that a photographic plate was affected by this substance whether or not the salt had been previously exposed to sunlight, thus indicating that the effect was a property of the normal atom. Further investigation showed that uranium was able to ionize the surrounding air. Since these effects could be reduced by covering the uranium with successively thicker amounts of some material, the emission of some sort of ray was suggested.

Following these discoveries, Mme. Curie observed[2] that the element thorium was likewise radioactive; further research of an extremely laborious nature resulted in the isolation in 1898 of two new radioactive elements, namely, polonium and radium, the latter being about a million times more active than an equal weight of uranium. Debierne, in 1899, succeeded in discovering still another radio element, which he named actinium,[1] while ionium was separated by Boltwood[2] in 1907.

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[1] Becquerel, *Comptes Rendus*, **122**, 420 (1896).

[2] Curie, *Comptes Rendus*, **126**, 1101 (1898); **127**, 175, 1215 (1898).

Investigation then went on apace, in the hands of Rutherford, Soddy, the Curies, and many others, resulting in the clarification of the many confusing aspects of the subject and leading to the present knowledge of radioactivity and nuclear structure. The most recent comprehensive treatment is that by Rutherford, Chadwick, and Ellis;[3] a briefer account is given by Hevesy and Paneth,[4] while a more specialized discussion of the recent work on the problems of nuclear structure is due to Gamow.[5]

The presence of a radioactive substance may be detected in several ways, though not all of them are equally sensitive or applicable in all cases.

1. Photographic action.
2. Production of scintillations of visible light on suitably prepared screens.
3. Ionization of a gas; used in the discharge of an electroscope or in the more complicated Geiger "counter," and also in the Wilson expansion chamber.
4. The emission of heat.
5. Chemical effects such as the decomposition of water.

These effects are due not actually to the mere presence of a radioactive element, but rather to the fact that it is disintegrating into another element; it is the small particles flying off with great energy that affect the detecting instrument. In some cases, the readjustment of the new atom to a state of stability releases a photon of high energy, which is also responsible for the physical effect. These projectiles resulting from a nuclear explosion have been shown to be separable into three classes with quite characteristic properties, the original distinction being based on their ability to penetrate matter.

α Rays will penetrate, on the average, several centimeters of air or a few thousandths of a centimeter of aluminium, after which their ability to affect any instrument ceases abruptly. This critical distance, generally given in centimeters of air at a specified temperature and pressure, is known as the "range," and is different for the α rays from various elements, but approximately the same for all the rays from a given substance. (See Sec. **10-15.**) These "rays" have been shown to be

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[1] Debierne, *Comptes Rendus*, **129**, 593 (1899).

[2] Boltwood, *Am. J. Sci.*, **24**, 370 (1907); *Physik. Zeits.*, **8**, 884 (1907).

[3] Rutherford, Chadwick, and Ellis, "Radiations from Radioactive Substances," Macmillan (1930).

[4] Hevesy and Paneth, "Radioactivity," Oxford University Press (1926).

[5] Gamow, "Atomic Nuclei and Radioactivity," Oxford University Press (1931).

doubly ionized helium atoms, *i.e.*, they are helium nuclei, traveling with velocities about one-thirtieth that of light.

β *Rays* are more penetrating; their effects, however, do not cease at a critical distance but decrease more or less exponentially. The distance in aluminium at which their influence drops to one-half its initial value varies roughly from a ten-thousandth to a few hundredths of a centimeter. The penetrating ability varies for the rays from different elements and frequently exhibits several values characteristic of each element. Such rays have been shown to be electrons ejected at speeds approaching that of light.

γ *Rays* are still more penetrating, their intensity falling off approximately exponentially with the distance, dropping to half value in from 0.02 to 7 cm. of aluminium. These rays are true electromagnetic waves, similar to light and X-rays, but with wave lengths of the order of from 1 Å to 0.0001 Å.

10-2. Disintegration.—The disintegration theory advanced by Rutherford and Soddy[1] in 1903 was able to account adequately for the observed changes in activity of a radioactive substance with the passage of time. Briefly stated, the theory is the following.

From time to time a certain definite fraction of the atoms becomes unstable (for some unknown reason), and a nuclear explosion results. Either an α or a β particle is expelled, depending on the type of atom in question. (A few elements may release either type of particle.) Since an α particle is a doubly ionized helium atom—*i.e.*, a helium nucleus—it consists of four protons and two electrons bound closely together, and hence has an atomic weight of 4, taking that of a proton as unity. After the expulsion of an α particle, therefore, the residue of the atom has an atomic weight 4 units less. Since the net charge of an α particle is $+4 - 2 = +2$ (taking the absolute magnitude of the electron's charge as unity), the residue has a net nuclear charge after the explosion that is $+2$ units less than before the disintegration, *i.e.*, the atomic number of the atom is reduced by 2. Thus a radium atom, of atomic weight $M = 226$ and atomic number $Z = 88$, becomes, after the loss of an α particle, an atom of radon with $M = 222$ and $Z = 86$. Two successive α losses cause the formation of radium A, $M = 218$ and $Z = 84$; and then radium B, $M = 214$ and $Z = 82$. When this latter atom becomes unstable, it loses a β particle from the nucleus; the mass of this electron being negligible, the residue (radium C) has the same atomic weight as its predecessor, $M = 214$, but the net positive charge of the nucleus is now increased by 1, so that $Z = 83$. Ra B and Ra C have therefore the same mass but different atomic numbers; this latter quantity determines the number of external orbital electrons and hence the chemical properties; such atoms of the same mass but different atomic

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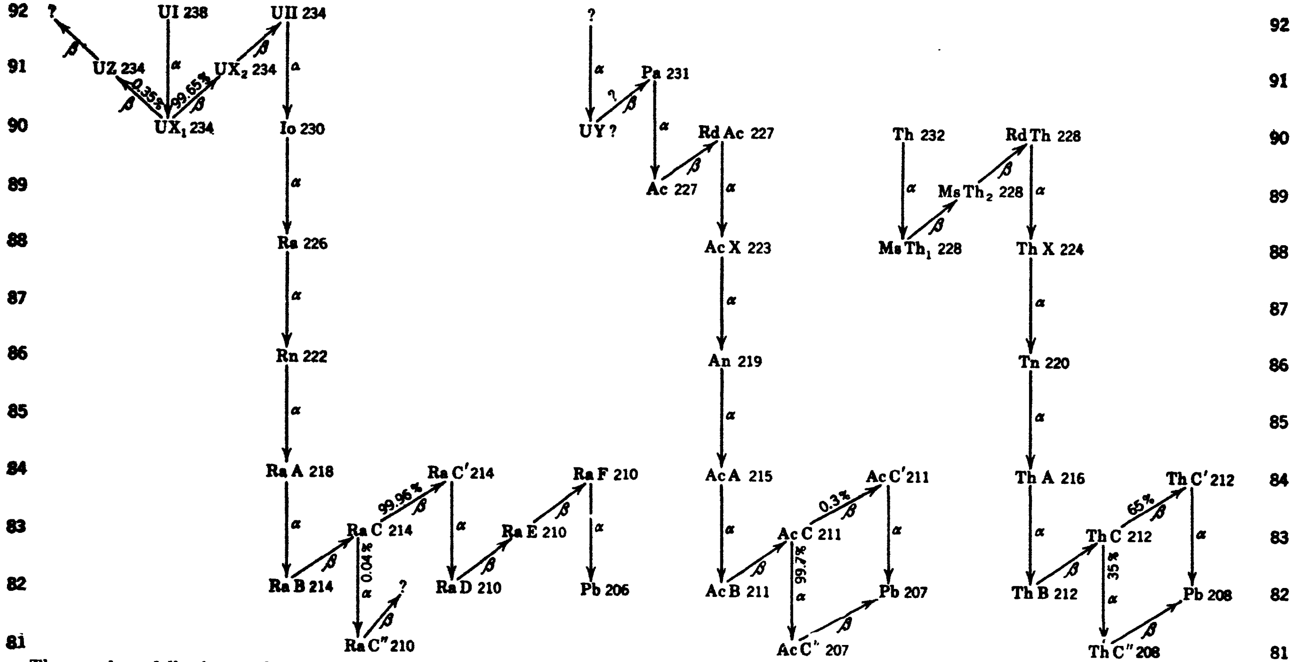
[1] RUTHERFORD and SODDY, *Phil. Mag.*, **5**, 576 (1903).

THE DISINTEGRATION SERIES OF THE RADIOACTIVE ELEMENTS



The numbers following each element denote the total number of protons in the nucleus; this is also the approximate atomic weight, neglecting the packing fraction.

The atomic numbers are given on the borders.

Substance	Symbol	Half life, T	Decay constant λ (sec.$^{-1}$)	α-Particle properties			
				Range (cm., 15°C.)	Vel. $\times 10^{-9}$ (cm. sec.$^{-1}$)	H r $\times 10^{-5}$ (gauss cm.)	Energy $\times 10^{-6}$ (electron volts)
Uranium I. . .	UI	4.4×10^{9} y	5.0×10^{-18}	2.73	1.41	2.91	4.05
Uranium X_1.	UX_1	24.5 d	3.28×10^{-7}				
Uranium X_2.	UX_2	1.14 m	1.01×10^{-2}				
Uranium Z. . .	UZ	6.7 h	2.87×10^{-5}				
Uranium II. .	UII	3×10^{5} y	7.4×10^{-14}	3.28	1.50	3.10	4.63
Uranium Y. .	UY	24.6 h	7.81×10^{-6}				
Ionium.	Io	8.3×10^{4} y	2.6×10^{-13}	3.19	1.48	3.07	4.55
Radium.	Ra	1,590 y	1.38×10^{-11}	3.39	1.51	3.13	4.74
Radon.	Rn	3.825 d	2.097×10^{-6}	4.12	1.61	3.34	5.44
Radium A. . .	RaA	3.05 m	3.78×10^{-3}	4.72	1.69	3.50	5.97
Radium B. . .	RaB	26.8 m	4.31×10^{-4}				
Radium C. . .	RaC	19.7 m	5.86×10^{-4}	4.1	1.61	3.34	5.44
Radium C′. . .	RaC′	ca. 10^{-6} s	ca. 10^{6}	6.96	1.92	3.98	7.68
Radium C″. .	RaC″	1.32 m	8.7×10^{-3}				
Radium D. . .	RaD	22 y	1.00×10^{-9}				
Radium E. . .	RaE	5.0 d	1.61×10^{-6}				
Radium F. . .	RaF	140 d	5.73×10^{-8}	3.92	1.59	3.29	5.25
Protactinium	Pa	3.2×10^{4} y	6.86×10^{-13}	3.67	1.55	3.22	5.01
Actinium. . . .	Ac	13.5 y	1.63×10^{-9}				
Radioactinium.	RdAc	18.9 d	4.24×10^{-7}	4.68	1.68	3.49	5.92
Actinium X. .	AcX	11.2 d	7.14×10^{-7}	4.37	1.65	3.41	5.66
Actinon.	An	3.92 s	0.177	5.79	1.81	3.75	6.82
Actinium A. .	AcA	2.0×10^{-3} s	3.74×10^{2}	6.58	1.89	3.91	7.41
Actinium B. .	AcB	36.0 m	3.21×10^{-4}				
Actinium C. .	AcC	2.16 m	5.35×10^{-3}	5.51	1.78	3.69	6.61
Actinium C′ .	AcC′	ca. 5×10^{-3} s	ca. 1.4×10^{2}	6.5 ?	1.9 ?	3.9 ?	7.3 ?
Actinium C″.	AcC″	4.76 m	2.43×10^{-3}				
Thorium.	Th	1.8×10^{10} y	1.2×10^{-18}	2.90	1.44	2.97	4.23
Mesothorium 1.	$MsTh_1$	6.7 y	3.26×10^{-9}				
Mesothorium 2.	$MsTh_2$	6.13 h	3.14×10^{-5}				
Radiothorium	RdTh	1.90 y	1.16×10^{-8}	4.02	1.60	3.32	5.35
Thorium X. .	ThX	3.64 d	2.20×10^{-6}	4.35	1.64	3.41	5.65
Thoron.	Tn	54.5 s	1.27×10^{-2}	5.06	1.73	3.58	6.24
Thorium A. .	ThA	0.14 s	4.95	5.68	1.80	3.72	6.74
Thorium B. .	ThB	10.6 h	1.82×10^{-5}				
Thorium C. .	ThC	60.5 m	1.91×10^{-4}	4.79	1.70	3.52	6.02
Thorium C′. .	ThC′	10^{-9} s ?	10^{9} ?	8.62	2.06	4.28	8.76
Thorium C″.	ThC″	3.1 m	3.73×10^{-3}				

Data taken from the Report of the International Radium Standards Commission, *Rev. Mod. Phys.*, **3**, 427 (1931), and from Rutherford, Chadwick, and Ellis, "Radiations from Radioactive Substances," Macmillan (1930).

number are known as isobars. When Ra C breaks up, 99.96 per cent of the atoms lose a β particle, becoming Ra C′, with $M = 214$ and $Z = 84$, while the remaining 0.04 per cent expel an α particle, giving rise to Ra C″, with $M = 210$ and $Z = 81$. Ra C and Ra C′ are isobars, whereas Ra C′ and Ra A are isotopes, since they have the same atomic number but different masses. Similar successive α and β losses eventually cause the formation of Ra G, $M = 206$ and $Z = 82$, which is an isotope of lead. This end product is stable.

There are two other disintegration series which break down in a similar manner; those of actinium and thorium, both of which end in stable isotopes of lead, with atomic weights 207 and 208, respectively. The three series are indicated in the accompanying table. It should be remarked that the indicated relationships of protactinium (Pa), UY and UZ are somewhat in doubt.

Having sketched the general types of disintegration of one atom into the next, it remains to discuss the important problem of the rate at which transformation takes place. As far as is known, there is no reason why any one atom should become unstable at any particular instant; the past history of the atoms, and in particular the fact that an atom may have remained stable for a long time, have no influence whatever on when disintegration will occur. The rule which has been found to agree with the experimental results is that for a given type of atom, the number of them that break up at any instant is proportional to the number present; that is, if there are N atoms of a certain element present at a time t, the rate of decrease, $-dN/dt$, is proportional to N, or equal to λN where λ is known as the *disintegration, decay* or *transformation* constant. Thus

$$-\frac{dN}{dt} = \lambda N \tag{10-1}$$

By integrating

$$\int \frac{dN}{N} = -\lambda \int dt$$

$$\log N = -\lambda t + C$$

If, when $t = 0$. $N = N_0$, then the integration constant $C = \log N_0$, and we have

$$N = N_0 e^{-\lambda t} \tag{10-2}$$

Thus the number of atoms remaining unchanged decreases rapidly at first, disintegration becoming less rapid as time goes on; a practically infinite time is required for the material to disappear completely. It is therefore convenient, when one wishes to indicate the rapidity of decay, to define the *period of half-life T*, or the time required for the number of atoms unchanged to be reduced to one half the initial value; that is,

$$\frac{N}{N_0} = \frac{1}{2} = e^{-\lambda T}$$

$$-\lambda T = \log_e\left(\tfrac{1}{2}\right) = 2.303 \log_{10}\left(\tfrac{1}{2}\right) = -0.693$$

$$T = \frac{0.693}{\lambda} \qquad (10\text{-}3)$$

Thus at the end of a time T, one half of the substance remains unchanged; 25 per cent is left in $2T$, 12.5 per cent in $3T$, 6.25 per cent in $4T$, and about 0.1 per cent in $10T$.

Since the disintegration of an atom is accompanied by the emission of an α or β particle capable of being detected by, say, an electroscope, the *activity*, or number of particles per second, is equal to the number of disintegrations per second. Hence, if we observe the activity due to a given number of atoms of some isolated substance such as polonium (Ra F), whose product is stable, the measured activity is directly proportional to the number of atoms still left unchanged. When the activity falls to half its original value, the half-period of the substance has been reached, and hence the disintegration constant can be computed from Eq. (10-3).

It is of interest to consider the situation known as *radioactive equilibrium*. If a quantity of UI is separated from its immediate product UX_1, the production of which is accompanied by the expulsion of an α particle, it is observed that the β-ray activity of the UX_1 drops exponentially, with a half-life period of 24.5 days. The UI, which lost all its β emission immediately after the separation, recovers to half its original β activity in the same interval, and has almost completely recuperated in 10 × 24.5 days, after which its β activity remains constant. This is an example of equilibrium between a very long-lived parent (UI, $T = 4.4 \times 10^9$ yr.) and a short-lived product (UX_1, $T = 24.5$ days). The explanation is quite simple. Due to its excessively long period, the number of UI atoms disintegrating every minute is to all intents and purposes a constant, so that UX_1 is being produced in the previously cleaned UI at a practically constant rate, accompanied by an α-particle emission. At first, the β activity, due to the breakdown of the UX_1 appearing in the UI is feeble, since but a few of these atoms are present, the number that disintegrate every second being proportional to those at hand. As the deposit accumulates, however, the decay increases in rapidity, until finally as many UX_1 atoms break up every second as are supplied from the UI. The β activity then remains constant (more exactly, it decreases with the extremely slow period of the UI), and equilibrium is said to exist, the ratio of UX_1 to UI atoms keeping a steady value. If N_1' is the number of UI atoms present in this equilibrium condition, and N_2' the number of UX_1 atoms, then the number of UX_1 atoms formed per second, being the same as the UI decaying, is given by

$N_1'\lambda_1$, where λ_1 is the disintegration constant of UI. The UX_1 atoms breaking up per second are $N_2'\lambda_2$, and, since in equilibrium these rates are equal, we have

$$N_1'\lambda_1 = N_2'\lambda_2$$

or (10-4)

$$\frac{N_2'}{N_1'} = \frac{\lambda_1}{\lambda_2}$$

Thus, in equilibrium, the ratio of the number of product to parent atoms is inversely proportional to their respective disintegration constants. This relation is of great use in determining the λ's of elements with half-life periods so long that no measurable decrease in their activity can be detected over the course of a few years. Often weighable quantities of the equilibrium constituents can be measured, so that the number of atoms N_1' and N_2' may be calculated from a knowledge of the mass of a single atom of each of the elements; then if the λ of the short-lived product is measured directly (by observing the time for it to fall to half activity), the disintegration constant of the other element can be computed from the above equation.

The mathematical representation of these ideas is not difficult. In the general case, if the number of atoms of the parent and product at any time t are given by N_1 and N_2, then the rate of increase of N_2 is given by the rate at which the parent decays ($N_1\lambda_1$), diminished by the rate at which the product breaks down ($N_2\lambda_2$); that is

$$\frac{dN_2}{dt} = N_1\lambda_1 - N_2\lambda_2 \tag{10-5}$$

The solution of this differential equation is of the form

$$N_2 = Ae^{-\lambda_1 t} + Be^{-\lambda_2 t}$$

where A and B are constants to be determined. If $N_2 = 0$ when $t = 0$, then $B = -A$, and we have

$$N_2 = A(e^{-\lambda_1 t} - e^{-\lambda_2 t}) \tag{10-6}$$

so, by differentiating

$$\frac{dN_2}{dt} = -\lambda_1 Ae^{-\lambda_1 t} + \lambda_2 Ae^{-\lambda_2 t} \tag{10-7}$$

But initially $dN_2/dt = N_1^0\lambda_1$, where N_1^0 is the number of atoms of the parent at time $t = 0$. Setting $t = 0$ in Eq. (10-7) and equating these two expressions for the initial increase in N_2, we have

$$N_1^0\lambda_1 = -\lambda_1 A + \lambda_2 A$$

or

$$A = \frac{N_1^0\lambda_1}{\lambda_2 - \lambda_1}$$

Therefore (10-6) becomes finally

$$N_2 = \frac{N_1^0\lambda_1}{\lambda_2 - \lambda_1}(e^{-\lambda_1 t} - e^{-\lambda_2 t}) \tag{10-8}$$

The time in which N_2 reaches a maximum value may be obtained by differentiating this expression with respect to t and equating to zero, which yields

$$t_{\text{max}} = \frac{1}{\lambda_2 - \lambda_1}\log_e\frac{\lambda_2}{\lambda_1} = \frac{2.303}{\lambda_2 - \lambda_1}\log_{10}\frac{\lambda_2}{\lambda_1} \tag{10-9}$$

If the product has a half-life period that is very much greater than that of the parent, so that $\lambda_2 << \lambda_1$, the first term in Eq. (10-8) soon becomes inappreciable and N_2 decays with a period characteristic of itself; while if the parent has a much longer life, $\lambda_2 >> \lambda_1$, and N_2 eventually breaks down at a rate determined by the decay of the parent. Thus the final decay rate is that of the longer lived of the two elements. Radioactive equilibrium is only permanent (a constant ratio of product to parent) when once attained, if the parent has the longer life, the product then breaking up as fast as it is formed.

We may apply these ideas to the preceding discussion of uranium I and uranium X_1. We were able to disregard the immediate products of UX_1, in discussing its β activity, for the following reasons. This substance decays, with β emission, with a half-life of 24.5 days, turning gradually into UX_2 with a half period of 1.14 min. Application of Eq. (10-9) shows that the maximum quantity of UX_2 is reached in

$$t_{\text{max}} = \frac{2.303}{1.01 \times 10^{-2} - 3.28 \times 10^{-7}}\log_{10}\frac{1.01 \times 10^{-2}}{3.28 \times 10^{-7}} = 1{,}022 \text{ sec.} = 17 \text{ min.}$$

Hence, after this short time, the total β emission from UX_1 and UX_2 will be determined by the period of the former. Other examples of these growth and decay processes will be considered in a later section.

10-3. The Range of α Particles.—The simplest, although the least accurate, method of observing the characteristic range of the α rays from a radioactive substance is by means of the fluorescence they produce on a zinc sulphide screen. As the number of atoms of, say, air between the source and screen is increased (either by moving the source or altering the pressure of the air), the scintillations are observed to cease quite abruptly at a distance that is characteristic of the α particles of the particular source used. As will be seen later, the velocity of an α particle is reduced by passage through matter, and at a critical velocity it is no longer capable of making its presence known. (This threshold value varies slightly with the means used to detect the particles, but for our purposes it may be taken as always constant.) Since the number of atoms per cubic centimeter in a gas varies directly as the pressure and inversely as the absolute temperature, through the relation $p = nkT$, the range determined under various conditions of p and T may be easily reduced to a standard situation, since the range is inversely proportional to n. The standard air pressure is always taken as 760 mm. Hg, but the standard temperature is variously taken as 0°, 15°, and 18°C.

The electrical method of determining ranges has been found much more satisfactory. The α particles travel with such velocity that they are able to ionize approximately 200,000 gas atoms through which they pass, and this relatively large charge may be detected by an electrometer or electroscope. A highly sensitive arrangement is that due to Geiger and Nuttall.[1] In the center of a hollow metallic sphere (of radius greater than the range at atmospheric pressure) is placed the radioactive source, the insulated support passing through a small hole in the sphere. The source and sphere are maintained at several hundred volts difference of potential and are connected to an electrometer which records the ionization current. As the gas pressure in the bulb is reduced, the α particles travel farther toward the wall before reaching their critical velocity but always producing the same number of ions. When the pressure has been lowered to such a degree that the particles reach the walls before ionizing their full quota of atoms, the ionization current becomes less and less. The change from the constant value of the current is quite abrupt, and observation of the pressure at which it occurs furnishes a very reliable means of obtaining the range.

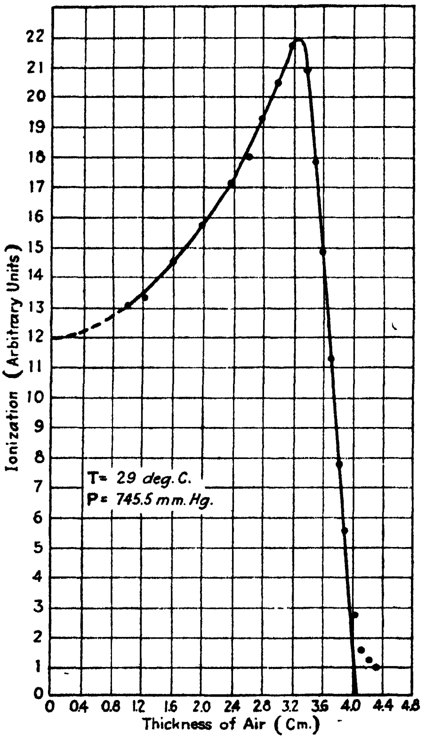


FIG. 10-1.—The experimental values of the ionization produced by α particles from polonium at various points throughout their range. A shallow ionization chamber, with copper gauze window, was used.

Perhaps the most common and illuminating method of measuring the range is by the use of a shallow ionization chamber, formed of a metal plate and a parallel metal gauze near it, the current being measured by an electroscope or electrometer. A narrow beam of α particles, defined by a slit system, is sent through the gauze, and the ionization due to that portion of the range between the gauze and back plate is observed by the rate of discharge of the recording instrument. It was with such an arrangement that Bragg and Kleeman[1] first observed the following phenomenon, not made clear by other methods. As the source is moved away from the ionization chamber, the current increases, slowly at first, and then rises rapidly to a maximum, falling away abruptly to zero as the critical range is reached. This is indicated by the curve of Fig. 10-1, obtained with a similar apparatus to be described later in more detail. It is thus apparent that the α particle is most efficient as an ionizer just before it is going so slowly that it ceases to ionize at all. The characteristic range is taken from the extrapolation of the steep part of the curve; the slight foot beyond this point is due to "straggling" of the α particles—irregular changes in velocity of some of them as they pass through the air. The significance of the shape of the curve will be discussed later.

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[1] GEIGER and NUTTALL, *Phil. Mag.*, **22**, 613 (1911); **23**, 439 (1912).

It is also possible to detect α particles by means of a Geiger counter and thus to determine their range. This instrument will be described more fully in a later section. Essentially, it consists of two electrodes in an enclosure, kept at a high potential difference. If a single α particle enters through a thin aluminium or mica window, a few ions are formed in the gas and these are rapidly drawn to the electrodes, causing the production by collision of still more ions in a cumulative process. In this way a relatively large current is initiated by the entry of a single ionizing particle, and this current may be recorded by an electrometer or amplified to operate a relay and mechanical counter. If the α-particle source is gradually advanced toward the window, the range in air may be taken as the point where the recorded impulses suddenly increase, correction being made for the "equivalent air thickness" of the window and for the stray counts observed when no radioactive material is present.

An extremely interesting method of making the path of an α particle visible is due to C. T. R. Wilson.[2] If moist air becomes supersaturated by rapid cooling (produced by suddenly increasing the volume of a chamber), any ions present become centers of condensation for water droplets. If an α particle passes through such a chamber, it produces roughly 200,000 pairs of ions before reaching the end of its range, and consequently the path is made visible for a good fraction of a second by the multitude of water droplets that condense on these ions. If a brilliant source of illumination is provided at the proper instant, the tracks can be photographed for permanent record. It is of particular interest to observe that the paths are almost always straight lines, showing that the α

[1] Bragg and Kleeman, *Phil. Mag.*, **8**, 719, 726 (1904); **10**, 318 (1905).

[2] C. T. R. Wilson, *Proc. Roy. Soc.*, **85**, 285 (1911).

particle passes undeflected through the atom which it ionizes. On very rare occasions, a direct collision with the nucleus of one of the gas atoms is made, and the α particle is deflected through a large angle. We shall return later to the significance of these extraordinary photographs of the collisions of individual atoms.

Many forms of Wilson expansion chambers have been made successfully. In all models some sort of piston is caused to be moved partially out of a cylinder with a glass window in the head; mechanical drive by gears or eccentrics has been used, but more satisfactory results are generally obtained when the region below the piston is suddenly connected to an evacuated tank by means of a valve. A detailed description of an automatic Wilson chamber and camera suitable for the investigation of artificial nuclear disintegration and similar research problems has been given by Blackett.[1] A simple and effective model has been described recently by Curtiss.[2] Very simple devices may be obtained commercially for visual demonstration; these consist of a glass chamber connected to a rubber bulb. Squeezing the bulb compresses the air above the liquid in the chamber and bulb, and when the latter is released, the expansion is sufficient to render visible the tracks from a radioactive source inside the chamber. It may be observed with such an instrument that the ranges of all the particles are the same, but any absolute measurement is hindered by lack of knowledge of the pressure conditions when the track was formed.

10-4. Ratio of Charge to Mass of an α Particle.—It was shown in 1903 by Rutherford[3] that α rays could be deflected by magnetic and electric fields, although with considerable difficulty, the direction of the deflection being concordant with the assumption that they were positively charged. The procedure was to allow the rays from an extended source to pass between a series of closely spaced parallel plates, a magnetic field being applied parallel to the plane of these plates. Because of the deflection, some of the particles struck the plates and were unable to enter the ionization chamber of an electroscope. The change in the rate of leak of the latter, at various field strengths thus permitted an estimate of the quantity $Hr = Mv/E$ [Eq. (4-10)], where M, E and v are the mass, charge, and velocity of the particle, and r the radius of curvature of its path in the field of H gauss. A similar experiment, in which alternate plates were charged electrostatically positive and negative, gave a value for Mv^2/E [see Eq. (4-4)], so that the quantity E/M could be determined.

With the preparation of stronger radioactive sources, it was later found possible to deflect with electric and magnetic fields a single narrow beam and to record the deflection photographically.[1] These experiments, of considerably greater accuracy, yielded the value $E/M = 5.1 \times 10^3$ e.m.u. per gram.

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[1] Blackett, *J. Sci. Instruments*, **6**, 184 (1929); *Proc. Roy. Soc.*, **123**, 613 (1929).

[2] Curtiss, *Bur. Standards J. Res.*, **8**, 579 (1932).

[3] Rutherford, *Phil. Mag.*, **5**, 177 (1903).

The possible implications of this were so well stated by Rutherford that it is worth while quoting his paper, in order to indicate the manner in which a variety of experiments can be brought to bear on one problem.

> The value of E/M for the hydrogen ion in electrolysis is known to be nearly 10^4. As the ion is supposed to be an atom with a positive charge, then the value of E/M for the atom is 10^4. The observed E/M for the α particle is about one-half this value. The density of helium has been found to be 1.98 times that of hydrogen, and, from observations of the velocity of sound in helium, it has been deduced that helium is monatomic. From this it is concluded that the helium atom has an atomic weight of 3.96. If a helium atom carries the same charge as the hydrogen atom, the value of E/M for the helium atom should consequently be about 2.5×10^3. If we assume that the α particle carries the same charge on the hydrogen ion, the mass of the α particle is twice that of the hydrogen atom. The value of E/M for the α particle may then be explained on three assumptions, namely, that the α particle is:
>
> 1. A molecule of hydrogen carrying the ionic charge of hydrogen.
> 2. A helium atom carrying twice the ionic charge of hydrogen.
> 3. One-half of the helium atom carrying a single ionic charge.

The first of these alternatives seemed unlikely, since helium rather than hydrogen had been found occluded in radioactive minerals;[2] the third required the *ad hoc* assumption of fractional atoms that combine together after being expelled. The second alternative appeared to be much the most reasonable and has been completely confirmed by subsequent more exact determinations of E/M by Rutherford and Robinson[3] and by Briggs,[4] and by the direct determination of the charge E by Geiger, as will be described presently. The final and conclusive evidence as to the nature of the α particle was supplied by the work of Rutherford and Royds.[5] They showed that if radium was imprisoned in a glass tube whose walls were too thick to permit the diffusion of helium atoms through them, but yet thin enough to allow the penetration of α particles, then the space between the thin tube and an enclosing heavy vessel became filled within an interval of several days with enough helium to permit its identification by spectroscopic means. The conclusion is thus irresistible that α particles are helium nuclei (helium atoms with a charge $+2e$), expelled with enormous energy from the nucleus of the parent atom. They presumably pick up two electrons and become normal helium atoms soon after their ionizing power has been lost. All the evidence indicates that the only difference between the α rays emitted from various elements is their initial velocity. The most probable value of the ratio of the charge to mass is:[1]

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[1] RUTHERFORD, *Phil. Mag.*, **12**, 348 (1906).
RUTHERFORD and HAHN, *Phil. Mag.*, **12**, 371 (1906).

[2] RAMSAY and SODDY, *Proc. Roy. Soc.*, **72**, 204 (1903); **73**, 346 (1904).

[3] RUTHERFORD and ROBINSON, *Phil. Mag.*, **28**, 552 (1914).

[4] BRIGGS, *Proc. Roy. Soc.*, **118**, 549 (1928).

[5] RUTHERFORD and ROYDS, *Phil. Mag.*, **17**, 281 (1909).

$$\frac{E}{M} = 4823.1 \pm 0.6 \text{ e.m.u. gram}^{-1}$$

10-5. The Number of α Particles Emitted per Second from a Gram of Radium.—The first estimate of this important constant was arrived at by Rutherford[2] in 1905. A known mass of radium bromide, freed of its products, was spread on a plate in an evacuated enclosure, and the current due to the emitted α particles reaching a collecting plate a few millimeters away in a vacuum was measured with an electrometer. A transverse magnetic field returned to their origin all electrons emitted by the collecting plate as a result of the α-ray bombardment. The assumption was then made that the charge on each α particle was the same as that of an electron (this we now know is incorrect; the charge is $2e$), the best value then available being 3.4×10^{-10} e.s.u. Dividing this into the observed current and multiplying by 2, to account for the particles sent in the other direction, gave the total number of particles emitted per second by the source used. From the known mass of the source and the atomic weight of radium and bromine, the number Q, emitted per second from a gram of pure radium, freed of its products, could be calculated.

A direct count of the particles was made by Rutherford and Geiger[3] in 1908 using a Geiger counter. Ra C was used as a source, the amount present being determined from its γ activity. The source was placed inside a long evacuated tube which terminated at the window of the counter chamber, and the distance from source to counter was varied until a convenient number of discharges per minute was obtained. Assuming a symmetrical emission of α particles, the total emission in all directions was computed from the known solid angle that the counter window subtended at the source.

Both of these methods have been repeated by a number of workers in recent times[4] (assuming a charge $+2 \times 4.77 \times 10^{-10}$ in the first procedure) with concordant results. Several less direct means have also been employed. It was observed by Curie and Laborde[5] in 1903 that radium is continually at a higher temperature than its surroundings, and by calorimetric measurement they found that 1 gram of radium in equilibrium with its products develops about 100 cal. per hour. This of course is due to the absorption of the kinetic energy of the emitted particles by the walls of the container. Thus if H is the measured heat, expressed in ergs, developed per second by a substance that emits a single group of α particles, then $H = Q \times Mv_0^2/2$. The mass M is known, and the initial velocity can be determined from the range, through Geiger's rule [see Eq. (10-11)] or from deflection experiments. Hence Q, the number of particles, may be computed.[1] Also, the volume of helium produced by 1 gram of radium in equilibrium with its products has been found[2] to be 156 mm.^{3} at normal temperature and pressure per year; the number of atoms per cubic centimeter of any gases at N.T.P. is known to be 2.7×10^{19} so that the number of helium atoms formed per second can be found. Since each of these is made from an expelled α particle that has picked up two external electrons, the number Q may be calculated. Finally, the amount of radon in equilibrium with 1 gram of its parent radium has been measured; this quantity is known as the *curie.* It occupies 0.66 mm.^{3} at 0°C. and 760 mm. Hg. The disintegration constant of radon may be observed directly, so that λ of radium can be calculated from the equilibrium condition of Eq. (10-4). The atomic weight of radium has been measured and found to be approximately 226, so that an atom of it weighs 226/1.0077 times as much as hydrogen, the mass of which is accurately known. Therefore the number of atoms in 1 gram of radium can be found, and on multiplying by λ, we obtain Q, for λ is the fraction of the atoms that break down with the emission of an α particle at any instant.

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[1] Birge, *Rev. Mod. Phys.*, **1**, 1 (1929).

[2] Rutherford, *Phil. Mag.*, **10**, 193 (1905).

[3] Rutherford and Geiger, *Proc. Roy. Soc.*, **81**, 141 (1908).

[4] Hess and Lawson, *Wien. Ber.*, **127**, 405 (1918).
Geiger and Werner, *Zeits. Physik*, **21**, 187 (1924).
Jedrzejowski, *Comptes Rendus*, **184**, 1551 (1927).
Braddick and Cave, *Proc. Roy. Soc.*, **121**, 367 (1928).

[5] Curie and Laborde, *Comptes Rendus*, **136**, 673 (1903).

The determination of this constant is therefore an excellent example of the interlocking relationships between the various quantities of atomic physics. Conversely, a determination of it by any one method permits the evaluation of the fundamental constants occurring in the others. Considering the opportunities for error in the many diverse ways of measuring Q, the agreement between them is surprisingly good. The accepted value is

$$Q = 3.70 \times 10^{10}\ \alpha \text{ particles sec.}^{-1}\text{ gram}^{-1}$$

of radium freed of its products. This same number of α particles, of course, is emitted by each of the substances, disintegrating with the emission of an α particle, in equilibrium with a gram of radium.

10-6. The Charge of an α Particle.—This quantity was successfully measured by Rutherford and Geiger[3] in 1908. The procedure was similar to that employed earlier by Rutherford in his attempt to find the number of α particles emitted per second from 1 gram of radium, as described briefly above; but instead of assuming the charge and calculating the number, in this case the number emitted was already known from the Geiger counter experiment, so that the charge per particle was found by dividing the total charge collected by the number of particles expelled. It was found that the charge was 9.3×10^{-10} e.s.u., which is almost exactly twice the absolute value of the electronic charge. This result constitutes very strong evidence that the α particle is really a doubly charged helium atom.

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[1] Rutherford and Robinson, *Phil. Mag.*, **25**, 312 (1913).

[2] Boltwood and Rutherford, *Phil. Mag.*, **22**, 586 (1911).

[3] Rutherford and Geiger, *Proc. Roy. Soc.*, **81**, 162 (1908).

10-7. The Number of Ions Produced by an α Particle.—An accurate determination of the number of ions of air produced by an α particle from Ra C′ was made by Geiger[1] in 1909. The total ionization current due to the first 0.4 cm. of path under standard conditions of temperature and pressure was measured by placing a known quantity of Ra C′ at the center of a spherical collecting electrode, evacuated to such a degree that the radius was effectively equivalent to 0.4 cm. at 760 mm. Hg. Then, by a refined design of ionization chamber of shallow depth, the relative ionization at different parts of the range was determined, as in Fig. 10-1. The ratio of the total area under the curve to that between the abscissas 0 and 0.4 gave the ratio of the total ionization to that in the first 0.4 cm. of the path. As this latter quantity had been measured, as described above, the total ionization or charge per second could be computed. Dividing by the charge on one ion gave the total number of ions produced per second, and as the number Q of α particles emitted per second from 1 gram of radium already had been determined, the number emitted from the known amount of Ra C′ could be calculated. Hence the number of ions produced within the range of a single α particle of Ra C′ could be found by dividing the total number of ions by this number of α particles. The values for e and Q were not very accurately known at the time, but using modern values for these constants, Geiger's result becomes

$$2.2 \times 10^5 \text{ pairs of ions formed by 1 } \alpha \text{ particle from Ra C}'$$

10-8. The Experimental Relation between Range and Velocity.—The velocity of an α particle at different portions of its path has been investigated by Rutherford[2] and more accurately by Geiger[3] and by Briggs.[4] With a knowledge of E/M, observation, by photographic or scintillation methods, of the deflection in a vacuum due to a known magnetic field yields the value of the velocity, through the relation $Mv^2/r = HEv$ or $v = HrE/M$ where r is the radius of curvature. As sheets of mica are placed over the source (which is equivalent to moving it farther away in air from the observing screen or photographic plate), it is found that the velocity continually decreases from the initial value v_0 at distance $x = 0$ to an effective value 0 at $x = R$, after which point the α particle is no longer detectable. The decrease is not linear but Geiger found that it could be well represented by the expression

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[1] Geiger, *Proc. Roy. Soc.*, **82**, 486 (1909).

[2] Rutherford, *Phil. Mag.*, **12**, 134 (1906).

[3] Geiger, *Proc. Roy. Soc.*, **83**, 505 (1910).

[4] Briggs, *Proc. Roy. Soc.*, **114**, 313, 341 (1927).

$$v^3 = a(R - x) \tag{10-10}$$

where a is a constant. Thus the velocity at any point on the path is proportional to the cube root of the distance the particle has yet to go. It has been found that this equation holds quite well for the initial velocities of emission of α particles from different sources, *i.e.*,

$$v_0^3 = aR \tag{10-11}$$

This expression, together with the determination of the total number of ions produced by an α particle of Ra C′, enables us to calculate this number for an α particle from any other source, if its range is known. Let us assume that the total ionization produced is proportional to the total energy of the particle (this is very nearly true); *i.e.*, $I \propto Mv_0^2/2$, so from the above relation

$$I \propto R^{2/3} \tag{10-12}$$

Knowing the total ionization for an α particle from Ra C′, that for an α particle of any other range is directly calculable.

The form of Eq. (10-10) suggested to Geiger that the ionization produced in a given distance should be proportional to the energy absorbed in the same region. Thus

$$i \propto \frac{d(Mv^2/2)}{dx} \propto (R - x)^{-1/3}$$

if we substitute for v^2 from Eq. (10-10). Hence

$$i^3 = \frac{c}{R - x} \tag{10-13}$$

where c is some constant. The plot of i against x gives a curve of the form shown in Fig. 10-2. This curve bears a striking resemblance to the experimental results, when it is remembered that for any real pencil of α particles, from a thick layer of radioactive material, the effective initial velocities are variously altered by absorption in the layer. This and local variations in density of the absorbing screens will tend to smooth out the curve.

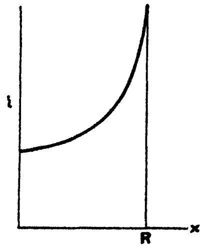

FIG. 10-2.—The calculated shape of the ionization current curve due to an α particle.

10-9. The Relation between Range and Disintegration Constant.—It was early observed that the α particles of greatest range, and hence of greatest energy, came from radioactive elements of shortest life, and an empirical relationship to describe this was proposed by Geiger and Nuttall[1] in 1911:

$$\log \lambda = A + B \log R \tag{10-14}$$

where λ is the disintegration constant and R the range. The constant B has the same value for the radium, thorium, and actinium series, while A is different for the different series but constant within any one. This relation is only approximate, a notable exception being AcX. Nevertheless, it has been of great value in obtaining an indication of the disintegration constant for extremely long- and short-lived elements whose ranges can be measured.

It was at once realized that this equation expressed some fundamental characteristic of the nucleus, but for a long time no satisfactory explanation was forthcoming. On the basis of classical mechanics, it was to be expected that something definite should happen in the nucleus to distinguish the instant at which disintegration occurs; there should be a mechanical reason for the explosion. The most obvious supposition was that some sort of continual drain of energy took place, until a critical unstable nuclear configuration was reached. Unfortunately the rate of decay does not increase with the age of the atom, as this hypothesis would lead one to expect. The advent of wave mechanics altered the picture, however, since probabilities take the place of mechanical causality. In 1928, Gamow[2] and, independently, Gurney and Condon[3] showed by quantum mechanics how the disintegration of a nucleus should be governed by chance, leading to the exponential law of decay and, in particular, to a theoretical reason for the Geiger-Nuttall relation.

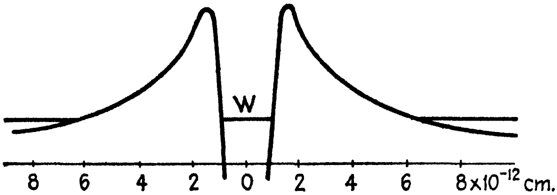

FIG. 10-3.—The probable shape of the potential barrier around a nucleus.

The problem is similar to that of the escape of an electron from a crystal lattice and involves the calculation of the probability that an α particle should tunnel through the potential barrier surrounding the nucleus. At great distances from the center there is an inverse square field of repulsion for a positively charged particle, but this must become an attractive force at very small distances, else the nucleus would fly apart at once. The curve of the potential energy against distance from the center of the atom must be somewhat as shown in Fig. 10-3. The chance that an α particle of energy W should penetrate the barrier depends on the shape of the potential wall and on the value of W. It has been shown that the slight variation in energy of emission of α particles from the different radio elements can account for variation in the period of half-life from 10^{-6} sec. to 10^{9} years, with the assumption of but a single shape of potential wall for all the elements. Although the problem is far from being solved in detail, quantum mechanics provides a very promising method of attack.

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[1] GEIGER and NUTTALL, *Phil. Mag.*, **22**, 613 (1911); **23**, 439 (1912).

[2] GAMOW, *Zeits. Physik*, **51**, 204 (1928).

[3] GURNEY and CONDON, *Nature*, **122**, 439 (1928); *Phys. Rev.*, **33**, 127 (1929).

10-10. The Charge and the Ratio *e/m* of β Particles.—The electronic nature of the β rays was established within a few years after the discovery of radioactivity. Giesel[1] in 1899 demonstrated that they were deflected by a magnetic field in the same sense as a negatively charged particle, while a year later the Curies[2] succeeded in intercepting enough β rays to show clearly their negative character. Becquerel[3] obtained an estimate of the ratio e/m by magnetic and electric deflection in 1900, while Wien[4] in 1903 made a first estimate of the magnitude of the charge. The more accurate determinations of e/m by Kaufmann,[5] Bestelmeyer,[6] and Bucherer,[7] to which reference has been made in Chap. IV, completely confirm the supposition that β rays are high-speed electrons, whose mass varies with their velocity in the manner prescribed by relativity.

10-11. The Origin of β Particles.—Although the physical characteristics of the β rays were soon established, the complex nature of their origin was for a long time a source of great confusion. Early work on the absorption of β rays by different thicknesses of matter indicated that they were absorbed almost exponentially, which at the time was considered as evidence that all the rays emitted from a single source were homogeneous in velocity; non-exponential absorption seemed to indicate a complex velocity distribution. These conclusions were vitiated by the work of W. Wilson,[8] who filtered out a homogeneous beam from a complex source by magnetic deflection and showed that this beam was absorbed practically linearly, thus suggesting that the apparent exponential absorption was an indication of a wide range of velocities.

The first semblance of order in this confusion was due to the work of von Baeyer, Hahn, and Meitner,[9] who showed by magnetic deflection that there were several distinct velocity groups in the β rays from mesothorium 2. A great improvement was obtained by the use of magnetic deflection instruments employing the 180° focusing property that has been described in connection with the Dempster mass spectrograph in Chap. IV. The radioactive source in the form of a fine wire is placed at the position of S_1 of Fig. 4-17 and the β rays are bent around in semicircles of various radii. They are recorded on a photographic plate in the plane defined by S_2 and S_3. This method was introduced in 1913 by Rutherford and Robinson,[1] who found a great many well-defined velocities in the β-ray spectra of RaB and C. Finally, Chadwick[2] found in 1914 that these sharp groups of velocities were accompanied by a β-ray spectrum with a continuous velocity distribution, over a very wide range.

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[1] Giesel, *Ann. Physik*, **69**, 834 (1899).

[2] Curie, *Comptes Rendus*, **130**, 647 (1900).

[3] Becquerel, *Comptes Rendus*, **130**, 809 (1900).

[4] Wien, *Physik. Zeits.*, **4**, 624 (1903).

[5] Kaufmann, *Physik. Zeits.*, **4**, 54 (1902); *Ann. Physik*, **19**, 487 (1906).

[6] Bestelmeyer, *Ann. Physik*, **22**, 429 (1907).

[7] Bucherer, *Ann. Physik*, **28**, 513 (1909).

[8] Wilson, W., *Proc. Roy. Soc.*, **82**, 612 (1909).

[9] von Baeyer, Hahn, and Meitner, *Physik. Zeits.*, **11**, 488 (1910); **12**, 273, 378 (1911); **13**, 264 (1912).

The recognition of these two distinct types of β-ray spectra—the *line* and the *continuous*, corresponding to definite velocities and to a distribution of velocities, respectively, led to the modern interpretation of the origin of β particles.

The *continuous β spectrum* is formed of the electrons emitted from the nucleus during the process of β disintegration. As yet, no final explanation has been given as to why these particles are ejected with a wide range of velocities; one would expect, *a priori*, a definite velocity or a group of them, analogous to the α-particle behavior, since the structure of the nucleus is presumably quantized; yet this does not seem to be the case. This continuous spectrum of the disintegration electrons forms the greater portion of the β emission of a radioactive element.

The *line β spectrum* is of a secondary origin and is due to the photoionization of the extranuculear electrons by collisions with γ-ray photons emitted by the nucleus after the original nuclear α or β expulsion, which leaves the nucleus in an unstable condition; in addition more external electrons may be removed by the action of the X-rays generated when the extranuclear electrons settle down to a state of stability. Thus a very complex line β spectrum can be produced, which is characteristic of the *product atom* formed after the original expulsion of an α or β particle from the nucleus of the parent. This highly important point—that the nuclear disintegration *precedes* any γ or secondary β emission—has been definitely settled by the work of Black,[3] Meitner,[4] Rutherford,[5] and Ellis and Wooster.[6] Nevertheless, the γ rays and the secondary line β spectrum are always referred to as being due to the parent rather than to the product, since the parent must be present, experimentally, if the spectrum is to be observed.

[1] Rutherford and Robinson, *Phil. Mag.*, **26**, 717 (1913).

[2] Chadwick, *Verh. Deut. Physik. Ges.*, **16**, 383 (1914).

[3] Black, *Proc. Roy. Soc.*, **106**, 632 (1924); *Proc. Camb. Phil. Soc.*, **22**, 838 (1925).

[4] Meitner, *Zeits. Physik*, **34**, 807 (1925).

[5] Rutherford, *Proc. Camb. Phil. Soc.*, **22**, 834 (1925).

[6] Ellis and Wooster, *Proc. Camb. Phil. Soc.*, **22**, 844 (1926).

10-12. The Line β Spectrum.—Let us examine in greater detail the mechanism of the emission of the extranuclear electrons as β particles. The initial process is the disintegration of the parent, due to an α or β expulsion; this usually leaves the product in a state of nuclear excitation, and a γ ray may be emitted, whose energy is presumably equal to the difference in energy between the excited and a stable nuclear condition. Thus γ photons of characteristic frequency may appear. In making their escape from the atom, some of them collide with the extranuclear electrons, most frequently with the low-lying ones in the K or L shells and cause their removal from the atom in the form of β rays. The kinetic energies of the latter are equal to that of the photon, diminished by the various works of ionization:

$$E_{\beta_1} = h\nu - K, \qquad E_{\beta_2} = h\nu - L, \qquad \text{etc.}$$

where K and L are the ionization energies of the electrons in the K and L shells of the product atom. These equations are recognized as similar to the Einstein photoelectric law. The validity of these expressions is proved by adding to the measured energies of selected groups of β rays the ionization energies obtained from X-ray absorption edges, thus obtaining a constant value for the energy of the γ-ray photon, in close agreement with that found from crystal-grating measurements of the wave length. Similarly, if a different γ ray is emitted of frequency ν', a set of β rays are generated with energies given by

$$E_{\beta_3} = h\nu' - K, \qquad E_{\beta_4} = h\nu' - L, \qquad \text{etc.}$$

The removal of the K, L, etc., electrons from the product atom initiates at once the X-ray spectrum of the product; some of these X-ray photons in escaping may eject less tightly bound electrons in the extranuclear structure, whose kinetic energies are then given by

$$\begin{aligned} E_{\beta_5} &= h\nu_K - L, \qquad & E_{\beta_6} &= h\nu_K - M, \qquad \text{etc.} \\ E_{\beta_7} &= h\nu_L - M, \qquad & E_{\beta_8} &= h\nu_L - N, \qquad \text{etc.} \end{aligned}$$

so that an exceedingly complicated β-ray spectrum can be produced, characteristic of the product.

There is, of course, the possibility that a γ ray may ionize a near-by atom of the original substance that has not yet disintegrated, thus causing β emission, characteristic of the parent material. With thin radioactive layers, the probability of this is exceedingly small, but as we shall see later, a similar situation can be made the predominant one by special disposition of the apparatus and is used very frequently to determine γ-ray wave lengths.

10-13. The Continuous β Spectrum.—This, as we have said, is due to the true disintegration electrons emitted from the nucleus as the primary act of a β transformation. A great many experiments have been performed to determine the number of these particles compared to the secondarily produced β rays that we have already discussed, the results showing that only one disintegration electron appears at each transformation and that only a few per cent of the total β radiation is due to the subsidiary electrons of extranuclear origin which exhibit the characteristic velocity spectra. As this great preponderance of disintegration electrons extends over a wide range of velocities for a given element, their absorption as a whole by matter might be expected to be approximately exponential, in agreement with observation.

The distribution of velocity of these β rays has been investigated by the magnetic deflection method, which shows that the upper limit of the energy range is fairly sharp, being different for the β rays from various substances. For those yet measured, the smallest upper limit is that of Th B, with an energy of about 0.3×10^6 electron volts, while the greatest is 3.15×10^6 volts, due to Ra C.[1] The data for the lower limits of the energies are very meager and uncertain; nothing definite is known for energies less than about 100,000 volts, so it is not known whether the lower limits of these continuous β spectra are zero or some finite values.

The existence of the continuous β-ray spectrum presents a very interesting problem. If the nuclei in the initial and final states have unique characteristic energies it is difficult to see how the transformation can take place with the emission of an electron which may have any energy lying in a continuous range. The first suggestion was that the electrons are all emitted with the energy of the observed maximum of the continuous spectrum and that the velocity distribution is caused by various unequal energy losses occurring between emission and observation of the electrons. This hypothesis was ruled out by the work of Ellis and Wooster[2] who measured calorimetrically the total energy absorbed by 1.3 mm. of lead surrounding a sample of Ra E which effectively emits only these nuclear electrons. They found that the energy per disintegration absorbed by the lead corresponds to the average energy of the continuous spectrum rather than to its maximum energy. This disposes of the possibility that the disintegration electrons are all liberated with the maximum observed energy and that the continuous distribution is introduced by unequal losses, unless this excess energy escapes through the lead calorimeter surrounding the radioactive substance. A theory along this line has been proposed by Pauli. He suggests the possibility that at a nuclear β disintegration a *light* neutron (a neutral particle with the mass of an electron) is also liberated. The energy of disintegration may be divided in any way between these two particles, and as the neutron can traverse many centimeters of lead with a small probability of absorption its energy would have escaped detection. The only other suggestion yet proposed is that the law of conservation of energy fails for nuclear processes.

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[1] GURNEY, *Proc. Roy. Soc.*, **109**, 540 (1925); **112**, 380 (1926).

[2] ELLIS and WOOSTER, *Proc. Roy. Soc.* **117**, 109 (1927).

10-14. γ-Ray Wave-length Measurements.—These highly penetrating rays were first detected by their action on a photographic plate by Villard[1] in 1900, who found also that they are undeviated by a magnetic field. Subsequent work supported the supposition that they are similar to X-rays, but certain of them have much higher frequencies. The early investigations were concerned largely with their ability to penetrate matter, and it was shown that the intensity, as measured by the ionization produced in a gas, varies almost exponentially with the thickness of matter traversed.[2] These results, however, depend to a large extent upon the disposition of the source, absorbing screen and detecting instrument, as scattered and secondarily produced γ and β rays will be recorded in varying amounts.

Estimates of the wave length of γ rays have been made by extrapolating to high frequencies the relation found to hold with X-rays between the absorption coefficient and the wave length.[3] As we have seen in the preceding chapter, the atomic absorption coefficient is represented by

$$\mu_a = \tau_a + \sigma_a \tag{10-15}$$

where τ_a and σ_a refer to photoelectric absorption and to scattering, respectively. An empirical form for the dependence of μ_a on λ and the atomic number Z, which has been found reasonably accurate for X-rays of short wave length is[4]

$$\mu_a = K'Z^4\lambda^3 + 0.8\sigma_0 Z \tag{10-16}$$

where σ_0 is the scattering due to a single electron according to classical electrodynamics, its value being

$$\sigma_0 = \frac{8\pi e^4}{3m^2c^4} = 6.63 \times 10^{-25} \tag{10-17}$$

Writing $0.8\sigma_0$ as k, the absorption coefficient per electron is then

$$\mu_e = \frac{\mu_a}{Z} = K'Z^3\lambda^3 + k \tag{10-18}$$

Since the wave length of γ rays is less than the K absorption edge, the constant K' is the same for all absorbing materials. It has been found that the absorption of γ rays is almost wholly due to scattering for light elements (the term $K'Z^3\lambda^3$ is negligible for small Z and λ), while both scattering and photoelectric absorption play a part when heavy materials are used. Hence we may say, approximately, if we observe the absorption in very light and very heavy metals, such as aluminium and lead, that

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[1] Villard, *Comptes Rendus*, **130**, 1010, 1178 (1900).

[2] Soddy and Russell, *Phil. Mag.*, **18**, 620 (1909); Russell, *Proc. Roy. Soc.*, **88**, 75 (1913).

[3] Kohlrausch, *Wien. Ber.*, **126**, 441, 683, 887 (1917); Ahmad, *Proc. Roy. Soc.*, **109**, 206 (1925).

[4] Compton, A. H., "X-rays and Electrons," pp. 60, 189, Van Nostrand (1926).

$$\begin{aligned}\mu_{e\text{Al}} &= k \\ \mu_{e\text{Pb}} &= K'Z^3_{\text{Pb}}\lambda^3 + k\end{aligned}$$

Hence

$$\mu_{e\text{Pb}} - \mu_{e\text{Al}} = K'Z^3_{\text{Pb}}\lambda^3$$

or

$$\lambda = \left[\frac{\mu_{e\text{Pb}} - \mu_{e\text{Al}}}{K'Z^3_{\text{Pb}}}\right]^{\frac{1}{3}} \tag{10-19}$$

where K' is taken from X-ray data.

Alternatively, for hard γ rays and a light-absorbing material, in which case only scattering plays an appreciable part, use has been made of an expression due to A. H. Compton:[1]

$$u_e = \sigma_e = \frac{\sigma_0}{1 + \dfrac{2h}{mc\lambda}} \tag{10-20}$$

More recently Klein and Nishina[2] have proposed a formula based on a relativistic treatment of quantum mechanics that is in somewhat better agreement with experimental data in the γ-ray region:

$$\sigma_e = \frac{6}{8}\sigma_0\left\{\frac{1+\alpha}{\alpha^2}\left[\frac{2(1+\alpha)}{1+2\alpha} - \frac{1}{\alpha}\log_e(1+2\alpha)\right] + \frac{1}{2\alpha}\log_e(1+2\alpha) - \frac{1+3\alpha}{(1+2\alpha)^2}\right\} \tag{10-21}$$

where $\alpha = h\nu/mc^2 = h/mc\lambda$. It should be noticed that both this and the Compton equation predict a constant value of the scattering per electron for a given wave length. Recent experiments by Meitner and Hupfeld,[3] Jacobsen[4] and by Tarrant and Gray[5] indicate that σ_e increases as the atomic number of the absorbing material is increased, if the usual assumption is made that σ_e is the total scattering divided by the number of extranuclear electrons, Z. It is not yet clear whether or not this anomalous absorption can be accounted for by assuming that some of the constituents of the nucleus assist in the scattering process. All estimates of wave length based on absorption measurements, give, of course, only the so-called "effective" or mean wave length of the stronger rays.

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[1] COMPTON, A. H., *Phys. Rev.*, **21**, 483 (1923).

[2] KLEIN and NISHINA, *Zeits. Physik*, **52**, 853 (1928).

[3] MEITNER and HUPFELD, *Zeits. Physik*, **67**, 147 (1931).

[4] JACOBSEN, *Zeits. Physik*, **70**, 145 (1931).

[5] TARRANT, *Proc. Roy. Soc.*, **135**, 223 (1932); TARRANT and GRAY, *Proc. Roy. Soc.*, **136**, 662 (1932).

Direct wave-length measurements of some of the softer γ rays from Ra B and C, by photographing the spectrum produced by diffraction from a rock-salt crystal, were first made by Rutherford and Andrade[1] in 1914, and investigations of this sort have been carried on for the hard nuclear rays by Thibaud[2] and by Frilley.[3] The technique is similar to that used with X-rays, but strong sources and long exposures are required, with special precautions to prevent fogging of the photographic plate by primary and secondary scattered β and γ rays. Kovarik[4] and Steadman[5] have varied the procedure for weak sources by detecting the diffracted rays with Geiger counters, by which means the measurements have been extended below 0.005 Å.

A more usual method[6] of determining the wave lengths of γ rays is by measuring the energies of the secondary β particles ejected from the extranuclear structure by the absorption of a γ ray. This has been referred to previously. The kinetic energy of the β rays is determined by magnetic deflection, and is given by

$$E_{\beta_1} = h\nu_1 - K; \qquad E_{\beta_2} = h\nu_2 - K;\text{ etc.}$$
$$E_{\beta_3} = h\nu_1 - L; \qquad E_{\beta_4} = h\nu_2 - L;\text{ etc.}$$

where E_{β_1} E_{β_2}, etc., are the measured energies of the β particles; ν_1 ν_2, etc., the frequencies of the γ rays; while K and L are the known energies of extraction of an electron from the K and L shells, found from X-ray absorption. Pairs or more of β rays are thus due to the conversion into β particles of γ rays of a single frequency.

A variation of this procedure is known as the *excited β-ray method.* Instead of observing the β particles ejected by photoelectric action from the same atom that emits the γ rays, these photons are allowed to fall on a target of some non-radioactive material whose X-ray levels are well known, the β rays emitted from this being analyzed magnetically. Thus, a small glass tube of the radioactive substance is surrounded with a thin sheath of, say, platinum, this combination being used as the source in a magnetic β-ray spectrograph. The energies of the particles are then given by

$$E_\beta = h\nu - W$$

where W is the known energy of extraction of an electron from the K, L, or M level of platinum. As ionization from the K level is several times more probable than from the L, observation of the intensities prevents serious uncertainty as to which level is effective. Any doubt can be removed by substituting some other metal for the target and observing the symmetrical shift of the β-ray energies.

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[1] Rutherford and Andrade, *Phil. Mag.*, **27**, 854 (1914); **28**, 263 (1914).

[2] Thibaud, *Comptes Rendus*, **179**, 1322 (1924); *J. Physique*, **6**, 82 (1925).

[3] Frilley, *Comptes Rendus*, **186**, 137 (1928); *Ann. Physique*, **11**, 483 (1929).

[4] Kovarik, *Phys. Rev.*, **19**, 433 (1922).

[5] Steadman, *Phys. Rev.*, **36**, 460 (1930).

[6] Ellis, *Proc. Roy. Soc.*, **101**, 1 (1922).

These photoelectric methods have extended the measurement of γ-ray wave lengths to much shorter regions than can be investigated by crystal gratings, the validity of the procedure being confirmed by the close agreement in the results for the region where the two methods overlap.

It should be observed that although many of the γ rays have their origin in the nucleus, some of them arise in the extranuclear electron structure, as secondary products of a nuclear γ ray, and are true X-rays, as described before.

10-15. Nuclear Structure.—As was mentioned in Chap. V, the experiments of Rutherford[1] on the scattering of α particles by thin films of matter could be explained if the atom were supposed to consist of a very small and consequently very dense nucleus bearing a net positive charge $+Ze$ and surrounded at relatively large distances by Z extranuclear electrons. This experimental knowledge of nuclear properties was a result of the discovery of radioactivity, but only indirectly, as this latter phenomenon was used only as a means of supplying very energetic particles which could approach so close to the nucleus as to be deflected from their path by its intense electric field. The disintegration of radioactive atoms, however, furnishes even more detailed knowledge of nuclear structure, for a consistent explanation of the observed phenomena can be obtained if it is assumed that the nucleus is made up of protons and combinations of protons and electrons in units of neutrons and possibly α particles. Both α particles and electrons (β particles) are emitted during the disintegration processes, but it is very unlikely that free electrons exist inside the nucleus. When their existence is postulated, many theoretical difficulties are encountered and the predicted nuclear properties are at variance with certain experimental results in the fields of molecular spectra and the hyperfine structure of spectral lines which are concerned with nuclear moments. The presence of protons and neutrons may be inferred from the presence of atoms whose atomic weights are not divisible by 4. Experimental verification of this inference has been supplied by the artificial disintegration and transmutation of non-radioactive substances when they are bombarded by α particles.

The experiments demonstrating the presence of protons were first performed by Rutherford[2] in 1919 and consisted in the observation, by the scintillation method, of particles of abnormally long range when various materials were subjected to the α-ray bombardment of radium. The elements for which these were found[1] were all those up to and including potassium, with the exception of hydrogen, helium, lithium, beryllium, carbon, and oxygen. Measurements by magnetic deflection indicated that the long-range particles were hydrogen nuclei, *i.e.*, protons. The interpretation was that about one out of every 100,000 α particles made such a direct collision with the nucleus of an atom that it was able to knock a proton out of it. The fate of the incident α particle was discovered by the expansion-chamber photographs of Blackett,[2] taken of the passage of α rays through nitrogen. Out of 23,000 pictures, including the tracks of 270,000 α particles, eight examples were found in which the track forked abruptly into two branches. Stereoscopic pictures were taken by two cameras at right angles, so that the true paths in space could be reproduced, and from the measurement of the angles it was found that momentum was conserved, although kinetic energy was not, if one of the tracks was assumed to be that of a proton and the other that of a particle of atomic weight 17. No traces were visible of the α particle after the collision, so it is reasonable to assume that it was captured by the nitrogen nucleus at the same time that a proton was driven out. The atomic weight of nitrogen is 14, that of an α particle, 4; then $14 + 4 - 1 = 17$. The atomic number of nitrogen is $Z = 7$, so that Z of the resulting nucleus is $7 + 2 - 1 = 8$, if no electrons are gained or lost. Nitrogen is therefore transmuted into an isotope of oxygen. This may be expressd in the following way:

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[1] RUTHERFORD, *Phil. Mag.*, **11**, 166 (1906); **21**, 669 (1911).

[2] RUTHERFORD, *Phil. Mag.*, **37**, 581 (1919).

$$\mathrm{N}^{14} + \mathrm{He}^{4} = \mathrm{O}^{17} + p \qquad (10\text{-}22)$$

where p represents the ejected proton.

These experiments have been confirmed and extended by a number of investigators,[3] generally by either the scintillation or Geiger counter method, the energy of the emitted proton being calculated from its range. In some cases kinetic energy is gained and sometimes lost, presumably at the expense of the internal excitation energy of the product nucleus; disintegration may occur with or without capture of the α particle.

The evidence for the existence of a closely associated proton and electron to form a neutron was not obtained until much later. Bothe and Becker[4] observed the presence of what they supposed to be γ radiation emitted by certain elements such as lithium, beryllium, and boron when bombarded by α particles from polonium. This radiation was further investigated by Curie[1] and by Webster[2] who found that it was more penetrating than ordinary nuclear γ radiation. If the effects observed were actually due to photons, their energy, estimated from their penetrating power, would correspond to approximately 10,000,000 electron volts. The penetrating power of the radiation from boron is so great that it is inappreciably absorbed by as much as 5 cm. of lead.[3] It was further found by Curie and Joliot[4] that when this radiation traversed matter containing hydrogen very fast protons were produced. If these were liberated by some mechanism analogous to the Compton effect, the exciting radiation in the case of beryllium must have possessed an energy corresponding to 50,000,000 electron volts. These energies are, however, larger than could be obtained from any reasonable processes of atomic disintegration or synthesis which could be occurring at collisions between α particles and beryllium or boron nuclei. Furthermore, the scattering of this very penetrating radiation does not agree with the predictions of the Klein-Nishina formula [Eq. (10-21)], as it almost certainly should if it were of the nature of γ radiation. The agency, whatever its nature, which was responsible for these effects was investigated by Chadwick[5] and Feather[6] using a Wilson chamber and they observed that it was capable of imparting momentum to an atom of the gas which lay in its path. From the lengths of the paths of the recoil atoms the amount of momentum transferred could be ascertained. It was found on the assumption of photons being responsible for the effects, that the momentum carried by the radiation was not a constant, but that larger values had to be assumed for this quantity at collisions with heavy atoms than at collisions with light ones. This was obviously unsatisfactory and led to the hypothesis, put forward by Chadwick, that the effects observed were due to neutrons rather than electromagnetic radiation. On the assumption of the existence of these uncharged particles composed of one proton and one electron, very intimately associated together and with linear dimensions of the order of 10^{-13} cm., all the experimental observations could be reconciled. Great penetrating power would be a characteristic of such a particle, for the electric field surrounding it would be negligible, and it is through the interaction of this field with that of the atoms of the absorbing substance that a particle's energy is dissipated. On the assumption of a mass of 1 unit (O = 16), and the conservation of momentum at impact, the momenta of the various recoil atoms observed with a Wilson chamber could be satisfactorily accounted for. The maximum energy imparted by a neutron from beryllium to a hydrogen nucleus at a collision has been observed to be about 5.7×10^6 electron volts. As the maximum momentum transfer takes place when the neutron is brought completely to rest, this gives us the energy of the neutron. Finally, if the observed effects were due to electromagnetic radiation, it would be expected that Compton recoil electrons would be observed and an experiment by Dee,[1] designed to detect interaction between the agency that is responsible for these effects and electrons, has led to a negative result.

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[1] Rutherford and Chadwick, *Phil. Mag.*, **42**, 809 (1921); **44**, 417 (1922); *Proc. Phys. Soc.*, **36**, 417 (1924).

[2] Blackett, *Proc. Roy. Soc.*, **107**, 349 (1925).

[3] Bothe and Fränz, *Zeits. Physik*, **49**, 1 (1928).
Fränz, *Zeits. Physik*, **63**, 370 (1930).
Bothe, *Zeits. Physik*, **63**, 381 (1930).
Rutherford and Chadwick, *Proc. Camb. Phil. Soc.*, **25**, 186, (1929).
Pose, *Zeits. Physik*, **64**, 1 (1930); **67**, 194 (1931).
Chadwick, Constable, and Pollard, *Proc. Roy. Soc.*, **130**, 463 (1931).

[4] Bothe and Becker, *Zeits. Physik*, **66**, 289 (1930).

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[1] Curie, I., *Comptes Rendus*, **193**, 1412 (1932).

[2] Webster, *Proc. Roy. Soc.*, **136**, 428 (1932).

[3] De Broglie and Leprince-Ringuet, *Nature*, **130**, 315 (1932).

[4] Curie, I., and Joliot, *Comptes Rendus*, **194**, 273 (1932).

[5] Chadwick, *Nature*, **129**, 312 (1932); *Proc. Roy. Soc.*, **136**, 692 (1932).

[6] Feather, *Proc. Roy. Soc.*, **136**, 709 (1932).

When the ionizing agencies emitted by beryllium under α-particle bombardment are investigated at various angles and through screens of lead of different thicknesses, it is found that, in addition to the very penetrating neutrons that are observed with greatest intensity in the direction toward which the α particles are moving, there is a certain amount of less penetrating γ radiation emitted symmetrically in all directions. This is the cause of the majority of the fast photoelectrons that have been detected by several observers. On the assumption of the equivalence of mass and energy through Eq. (1-31), $E = mc^2$, the energy equations of the interaction of an α particle with a beryllium or boron nucleus may be written as follows:

Reaction

$$Be^9 + He^4 = C^{12} + n^1 + \gamma \tag{10-23}$$

Energy equation

$$M_{Be} + M_{He} + E_\alpha = M_C + M_n + E_C + E_n + h\nu \tag{10-24}$$

and reaction

$$B^{11} + He^4 = N^{14} + n^1 + \gamma \tag{10-25}$$

Energy equation

$$M_B + M_{He} + E_\alpha = M_N + M_n + E_N + E_n + h\nu \tag{10-26}$$

where n^1 stands for neutron, and γ for the γ radiation. The superscripts are atomic weights, and M and E are the mass energy and kinetic energy corresponding to the subscripts. The observed energies of the neutrons and the radiation are quite consistent with the energies available from the known masses of the atoms appearing in the equations. From the observations on recoil atoms it appears that the neutrons are liberated with energies lying in the continuous range below the limits imposed by $h\nu = 0$ in Eqs. (10-24) and (10-26). That is, the energy liberated at these processes may be apportioned in any way between n^1 and γ, the fastest neutrons being produced when no energy is emitted in the form of radiation. The limiting reaction, for which $h\nu = 0$, involving boron may be used to determine the mass of the neutron with the accuracy to which the other masses are known. For we have $M_{\mathrm{B}^{11}} = 11.00825$, $M_{\mathrm{He}^4} = 4.00106$, $M_{\mathrm{N}^{14}} = 14.0042$, and $E_\alpha = 5.25 \times 10^6$ electron volts = 0.00565 mass unit.

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[1] Dee, *Proc. Roy. Soc.*, **136**, 727 (1932).

$$\left(1 \text{ electron volt} = \frac{4.77 \times 10^{-10}}{300} \text{ erg} = \frac{4.77 \times 10^{-10}}{300 \times 9 \times 10^{20}} \text{ gram} = \frac{4.77 \times 10^{-10}}{300 \times 9 \times 10^{20} \times 1.649 \times 10^{-24}} \text{ mass unit} = 1.072 \times 10^{-9} \text{ mass unit}\right)$$

(The mass of a particle of unit atomic weight is the reciprocal of Avogadro's number: $1/N = 1.649 \times 10^{-24}$.) The maximum value of the energy of the neutron E_n, as found from the length of tracks in recoil experiments, is 0.0035 mass unit. Application of the conservation of momentum to the nitrogen atom and neutron formed from boron indicates that the energy of the nitrogen E_N is 0.00061 mass unit, taking the mass of the neutron as approximately unity. Equation (10-26) then permits (if $h\nu = 0$) a more precise calculation of this mass; *viz*, M_n = 1.0067 mass units. As we have seen in Sec. **4-18,** this leads to a binding energy of about 10^6 electron volts for a neutron.

Disintegration processes which are the reverse of such equations as Eqs. (10-23) and (10-25) have also been observed. Feather[1] has found that the nuclei of atoms of nitrogen and oxygen may capture a neutron at a collision and emit an α particle in accordance with the following equations:

$$\mathrm{N}^{14} + n^1 = \mathrm{Be}^{11} + \mathrm{He}^4 \tag{10-27}$$

$$\mathrm{O}^{16} + n^1 = \mathrm{C}^{13} + \mathrm{He}^4 \tag{10-28}$$

There is also evidence that nitrogen may be disintegrated without capturing the neutron but the exact process which takes place is less certain.[2]

Also, quite recently artificial disintegration has been accomplished by bombarding atoms with protons accelerated by several hundred thousand volts. Cockcroft and Walton[3] in this manner drove a proton into a lithium atom ($Z = 3$), with the result that it split up into two helium nuclei as shown by the following relation:

$$\mathrm{Li}^7 + p = 2\mathrm{He}^4 \tag{10-29}$$

The laboratory production of very high speed protons thus promises to supply a powerful means for investigating nuclear structure, since protons appear to be more efficient as disintegrators than α particles, and moreover they can be supplied in quantities equivalent to the α rays from enormous amounts of radium and at any chosen speed.

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[1] Feather, *Proc. Roy. Soc.*, **136,** 709 (1932); *Nature*, **130,** 237 (1932).

[2] For a detailed account of the experimental and theoretical knowledge in regard to the neutron, the reader is referred to Curie and Joliot, "L'Existence du Neutron," and Destouches, "Théorie du Neutron," Hermann et Cie. (1932.)

[3] Cockcroft and Walton, *Proc. Roy. Soc.*, **137,** 229 (1932).

These disintegration experiments have shown quite clearly what units of matter it is reasonable to assume are present in an atomic nucleus. The mechanism by which these particles are held together and the energies corresponding to different nuclear configurations are but little understood. A very interesting first attempt to consider the structure of a nucleus composed of neutrons and protons has been made by Heisenberg.[1] Its preliminary successes give great promise that a satisfactory theory of nuclear structure may be reached along these lines. There is also a certain amount of experimental evidence in regard to the energy relations within a nucleus. By analogy with the more familiar phenomena of the extranuclear electron structure the emission of electromagnetic radiation (nuclear γ rays) strongly suggests the existence of energy levels, or certain allowed configurations of the units composing the nucleus, which have characteristic energy contents.

Not only can nuclear energy levels be inferred from the supposition that the transfer of some particle from a high to a lower state causes the emission of a γ ray, but direct evidence is supplied from what is called the "fine structure" of α particles. Rosenblum[2] has observed, by magnetic deflection, that Th C emits α particles, in addition to the usual type, in five weak groups of different energies. The fine structure of α rays from Ra C and Ac C has also been observed by Rutherford, Ward, and Wynn-Williams[3] using a differential ionization chamber method, and two groups of α's from Rd Ac have been observed by I. Curie[4] with a Wilson chamber. These different groups are supposedly due to ejection of α particles from excited nuclei or with an accompanying excitation of the product nucleus and, hence, have different energies from the main body of the α rays, for which all of the energy of disintegration appears as kinetic energy of the particles emitted by a transformation from one normal nucleus to another. Consequently, the differences between the energies of the normal α rays and these other particles should give the energy values of excited states of the nucleus above its normal condition and, hence, might be expected also to correspond to the energies of some of the measured γ rays. These predictions have been substantiated, with surprisingly small margins of error.[5]

The discovery of a few α particles of abnormally long range from Th C was made by Rutherford and Wood[6] in 1916 by the scintillation method. These, and similar particles from Ra C, have been subsequently investi-

[1] HEISENBERG, *Zeits. Physik*, **77**, 1 (1932); **78**, 156 (1932).

[2] ROSENBLUM, *Comptes Rendus*, **190**, 1124 (1930); *J. Physique*, **1**, 438 (1930).

[3] RUTHERFORD, WARD, and WYNN-WILLIAMS, *Proc. Roy. Soc.*, **129**, 211 (1930).

[4] CURIE, I., *J. Physique*, **3**, 57 (1932).

[5] ELLIS, *Proc. Roy. Soc.*, **136**, 396 (1932); **138**, 318 (1932).

[6] RUTHERFORD and WOOD, *Phil. Mag.*, **31**, 379 (1916).

gated and found to consist of several distinct groups. A proposed explanation is that a nuclear proton in an excited level transfers its energy to an α particle just about to depart, so that the excesses of energy of these particles over the usual amount represent the energies of the nuclear levels above the normal state. Also certain experiments on the emission of protons by aluminium and fluorine nuclei under α-particle bombardment indicate the existence of resonance phenomena analogous to those which are familiar in the case of the extranuclear electron structure.[1] For the developments in the theory of nuclear structure since the publication of Gamow's book[2] the reader is referred to the discussions of Rutherford[3] and Ellis.[4]

10-16. Experiments on α-particle Ranges. *Scintillation Methods.*—Fluorescent screens may be prepared by depositing phosphorescent zinc sulphide, either alone or mixed with calcium tungstate, on to a glass plate. This should be first given a light coat of water glass (sodium silicate) or of Duco cement thinned down with amyl acetate. When this is almost dry so that the crystals do not sink under it, the fluorescent powder is sifted on to it by gently tapping a fine-mesh gauge on which a small pinch of powder has been placed. The coating should not be more than one crystal deep, else the light flashes will be obscured. This is assured by erring on the side of too sparse a surface density rather than too heavy a one.

The simplest arrangement is to observe ranges at atmospheric pressure by advancing the source in small steps up toward the prepared side of the screen and observing the scintillations with a magnifying glass or low-powered microscope from the other side. The source may be a small metal disk on which the active substance has been deposited. A simple mounting is to wax this plate on to the movable leg of a spherometer which is held in place by a clamp on the frame. The scale furnishes relative positions, and a cathetometer (or ruler, for rough work) is used to find the absolute distance from source to screen at any one setting.

Alternatively, the range may be observed at reduced pressure. The source is mounted inside a metal or glass tube, at a distance somewhat greater than the atmospheric range from one end; to this end is sealed the fluorescent screen with wax. A side tube leads to a manometer, rough vacuum pump, and stopcocks, to permit air to be admitted to or withdrawn slowly from the chamber. Knowledge of the distance from source to screen, and observation of the pressure at which the scintillations begin or disappear permit the calculation of the range at standard pressure, as described previously.

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[1] Pose, *Zeits. Physik*, **64**, 1 (1930); **67**, 194 (1931); **72**, 528 (1931). Diebner and Pose, *Zeits. Physik*, **75**, 753 (1932).

[2] Gamow, "Atomic Nuclei and Radioactivity," Oxford University Press (1931).

[3] Rutherford, *Proc. Roy. Soc.*, **136**, 735 (1932).

[4] Ellis, *Nature*, **129**, 674 (1932)

Scintillation observations must be carried out in a dark room, and it is necessary for the eyes to become accustomed to the darkness for a period of from ten to thirty minutes, depending on the individual, before the scintillations can be seen with ease. As the scintillations are faint, a microscope of large numerical aperture should be used; an 8-mm objective and 1.5 × ocular combination is satisfactory. Readings of the scales and pressures should be performed by an assistant, with the aid of a carefully shaded lamp. It is often a help in keeping the eye focused on the scintillations to illuminate the screen with a very feeble light; a small flash-light bulb, barely glowing with the current from a dry cell and control resistance, may be mounted at the end of a tube of black paper several inches long, the open end being next the screen.

Electroscope Method.—A much more satisfactory means of measuring the range of α particles is to observe the rate of discharge of an electroscope due to the air ions formed by the particles, the source being moved away in small steps.

The electroscope may consist of a metal case from the top of which is supported a flattened brass rod, which is insulated from the case by a plug of amber or sulphur. (The latter may be cast in place by heating the sulphur in a small dish to about 120°C. and pouring it into a mold about the supporting rod.) A rectangular piece of gold or aluminium foil is fastened at one end to the middle of the rod with a drop of varnish or saliva, so that, when a difference of potential is applied between the case and rod, the foil becomes charged with the same sign as the rod and is consequently repelled by it. Air ions of opposite sign are attracted to the foil or its support and neutralize some of the charge, so that the leaf falls slightly. The motion of the leaf is observed with a low-power microscope containing a graduated scale at its focal plane. The ionization current, measured by the rate of discharge of the electroscope, is then proportional to the reciprocal of the time for the leaf to move across some standard number of scale divisions. It is advisable always to use the same range of the scale as the rate of fall generally is not uniform throughout. The number of divisions to be adopted as unity should be large enough so that with a maximum rate of discharge accurate measurements can be made with a stop watch. An examination of the rate of fall at different parts of the scale may be made in order to see if the scale range may be reduced to, say, one half (and the corresponding times multiplied by 2) when observing very weak activities. The electroscope should always be kept charged for about ½ hr. before beginning observations, in order that any insulation losses may reach a steady value. The so-called *natural leak,* when no radioactive preparations are near by, is due to faulty insulation or to residual ions in the atmosphere. It should be observed before and after observations are made (and at intermediate times if the weather is moist), and the reciprocal of the time for the leaf to fall the standard distance should be subtracted from the reciprocal of the times determined during the experiment. These corrected values are taken as the activity, in arbitrary units.

A charging potential of 200 volts is generally adequate. One side of the line is connected to the case through a megohm resistance to guard against a heavy current if a short circuit is made accidentally, while the other wire is brought into contact with the leaf support when charging is desired. This contact may be made with a rod rigidly attached to the leaf support and passing out of the container through a tubular extension on the side. A metal cap should be placed over this collar after the charging has been accomplished, to keep stray ions from entering the chamber. An alternative method is to provide a bent metal rod, passing through an insulating bearing in the side of the box; by twisting this, it may be made to touch the foil support.

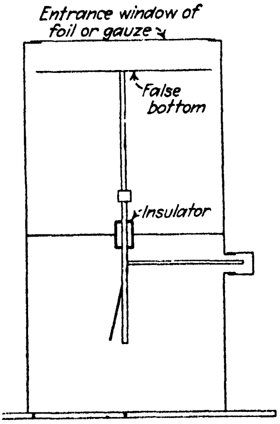

Fig. 10-4.—A diagram of an electroscope suitable for radioactive measurements.

When observing the α-particle ranges in metals, such as thin sheets of aluminium, the radioactive preparation may be placed in the bottom of the case and successive sheets of metal laid over it, though not in contact with the source, so that the foils do not become contaminated. To determine ranges in air, the bottom of the case may be made of a thin sheet of aluminium or of copper gauze and the source brought up in steps from below. It has been found more convenient, however, to build the electroscope with two chambers, as in Fig. 10-4. The lower one contains the leaf, the supporting rod passing up through an amber or sulphur insulating bushing into the ionization chamber above. The top of the latter is covered with copper gauze or aluminium foil, and the effective depth of this chamber may be altered by supporting a metal false-bottom plate on rods of different lengths which screw on to the leaf support. The active source is then brought down from above. This design permits changing the capacity of the instrument to suit weak or strong sources, and with an additional attachment it may be used to measure radioactive gases. For this purpose a metal tube 1 ft. long and about 1 in. in diameter is supported over the electroscope, in electrical contact with the case. A heavy wire is located along the axis of the tube by a support that emerges through an insulating bushing in the side. Metallic connection is made between this support and the rod to which the leaf is attached. The radioactive gas is allowed to flow into the tube through short pipes at its ends.

Let us examine what effect the shape of the ionization chamber will have on the ionization curve. Primarily, it is desirable that the same number of ions enter the chamber at all distances of the source, so that no correction for the inverse square law need be applied; this requires the entrance area of the chamber to be so large that the cone of α rays leaving the source shall lie within it at the maximum range. (The source may be an activated circular plate about 5 mm. in diameter at the end of a hollow lead tube about 1 cm. long, which thus defines a cone of about 45° apex angle.) In the second place, it is desirable that the depth of the ionization chamber be quite small—only a few millimeters from the entrance gauze or foil to the back plate. This, of course, reduces the intensity of the recorded current but permits the relative number of ions formed in small intervals of the total path to be determined; the shallower the chamber, the more closely can the ionization at various points of the range be determined. This ideal condition obviously cannot hold at distances greater than that at which the range of the particle just carries it to the back plate of the chamber. As the source is moved farther away, ions are formed over a smaller and smaller path within the chamber, so, other things being constant, the observed current toward the end of the range must necessarily decrease very rapidly. As an extreme case, if the depth of the chamber were greater than the range of the particle, the current would have a maximum value when the source was next to the entrance gauze, and would drop off steadily as the distance was increased. A compromise must therefore be reached, depending on the strength of the source available: one should use as shallow a chamber as possible consistent with ionization currents that take a reasonable time to record.

The shape of the very end of the ionization curve is further influenced by the fact that the end of the cone of rays is spherical in shape while the entrance to the chamber is flat, so that all of the ions are not recorded at extreme distances. This error can be avoided by using a spherical entrance window, but the correction is not very large. The use of a thin aluminium foil as an entrance window rather than a gauze is somewhat better, as then ions formed outside the chamber cannot drift in. Correction for this foil must be made by again determining the range with two foils in place, to see how much the range is reduced by the presence of one of them. The distance in air by which the foil reduces the range is known as the *stopping power* of the particular foil. The *equivalent absorbing power* is the thickness of foil that reduces the range by 1 cm. of air. The so-called "straggling" of α particles, which accounts for the foot of the curve when instrumental errors have been eliminated, need not be gone into here; there is a certain chance that some of the particles will lose less energy by collisions than will the average particle, so that they will advance farther. This has been investigated in detail by Henderson.[1]

10-17. Experiments on the Absorption of β and γ Rays.—The electroscope described above may be used for rough determinations of the absorption coefficients of β and γ rays, subject to the uncertainties, mentioned before, of the secondary rays scattered from the absorbing material, the electroscope itself, and near-by bodies. It is desirable, if possible, to surround the sides of the instrument with lead shields to reduce the effect of scattered γ rays, when measuring γ radiation, and to line it with paper or cardboard in order to absorb secondary β rays emitted by the walls.

The source, such as a small quantity of a radium salt, is mounted several centimeters above the ionization chamber, the window of which is closed with a gauze or thin aluminium foil. The chamber should be adjusted for its maximum depth to increase the sensitivity. Successive sheets of aluminium or lead are placed over the window and the rate of discharge of the electroscope noted.

The theory and the experimental data on the absorption and scattering of β particles are not in very good accord, largely due to experimental difficulties and the inherent complexity of the phenomena. As it is so light, the β particle is easily deflected from its path (as is shown by the tortuous tracks it leaves in an expansion chamber), so that it is very difficult to separate the effects of true absorption of its energy by ionization from its removal from the beam by scattering. We shall not go into the problem of "single," "plural" and "multiple" scattering, which are treated at length in the literature.[2]

Similarly, the analysis of γ rays from a study of their absorption is beset with many difficulties. Not only are the effects of photoelectric absorption and scattering both present, but they vary in different materials. Thus in light metals, such as aluminium, the absorption is almost wholly due to scattering, whereas in lead both phenomena are present, so that no simple correlation can be made respecting the separate components found with different absorbers. Moreover, in the scattering process, the wave lengths of the photons are shortened by the Compton effect, so that an originally homogeneous beam is soon degraded into many components. An account of the various experimental methods that have been used to separate these different effects may be found in the references that have been cited.

Since both β and γ rays are absorbed more or less exponentially, as a result of the variety of complicating factors, the experimental curve should follow the equation

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[1] Henderson, *Phil. Mag.*, **42**, 538 (1921).

[2] Rutherford, Chadwick, and Ellis, "Radiations from Radioactive Substances," Macmillan (1930).

$$I = I_1e^{-\mu_1x} + I_2e^{-\mu_2x} + I_3e^{-\mu_3x} + \cdots$$

where the I's are the initial ($x = 0$) intensities of the various components of the beam, the μ's are their respective absorption coefficients, and x is the thickness of the absorbing screen (see Sec. **9-9**). If the μ's are very different for the separate components, say, $\mu_1 << \mu_2 << \mu_3$, etc., it is possible to find the values of these quantities from the experimental data. The method is, briefly, to neglect all but the component of smallest μ for large values of x; *i.e.*, for large values of x, $I = I_1e^{-\mu_1x}$. The quantities μ_1 and I_1 may then be found by plotting the last portion of the curve for log I against x, which should give a straight line of slope $-\mu_1$, and intercept log I_1. The exponential term $I_1e^{-\mu_1x}$ is then subtracted graphically from the curve of I against x or algebraically from the experimental values of I at the various values of x. The resultant current

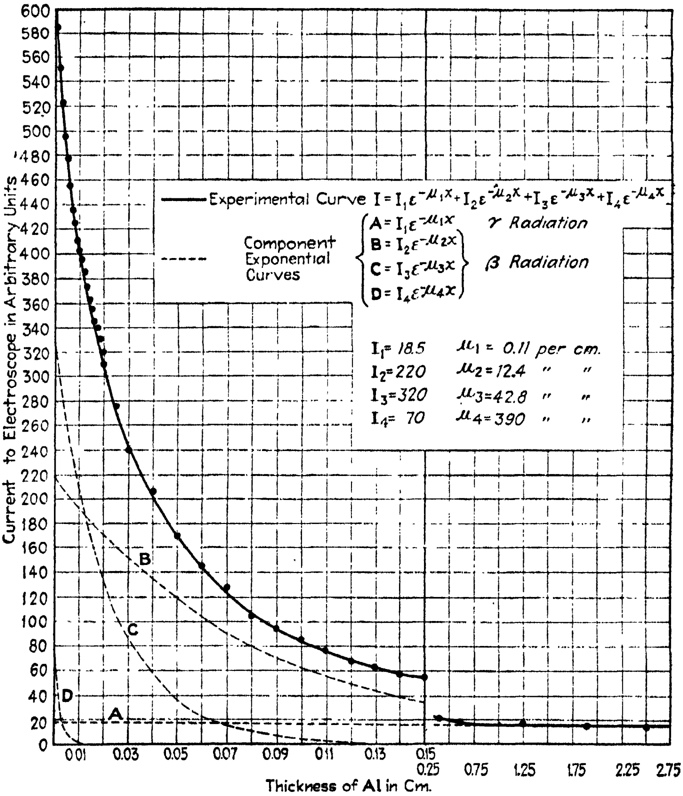

FIG. 10-5.—The absorption of β and γ rays from radium, in equilibrium with its products, by different thicknesses of aluminium.

$$I^1 = I - I_1e^{-\mu_1x} = I_2e^{-\mu_2x} + I_3e^{-\mu_3x} + \cdots$$

is then analyzed in a similar manner for μ_2 and I_2. In this way all the

μ's and I's may be found. The accuracy with which these quantities can be determined is not great, owing to the influence of various geometrical factors always present in absorption measurements and to the difficulty in determining the slopes and intercepts on the semilogarithmic plots. The heavy curve of Fig. 10-5 is a plot of the experimental values of I against x obtained with the β and γ rays from a small quantity of radium in equilibrium with its products. The broken-line curves represent the separate exponential components obtained by the method that has been outlined. Which portions of these curves are due to β and which to γ rays may be found by a second experiment, in which the source is placed between the poles of an electromagnet. The fastest β particles of appreciable intensity from a radium source are those from the line spectrum of Ra C, with an energy corresponding to a value of $Hr =$ 5,000 gauss-centimeters; a magnetic field of 1,400 gauss is adequate to keep these particles moving in circles between pole pieces of 3.5-cm. radius, if the source is at the center of the poles. A very few of the β particles have energies exceeding this amount, but no great ionization is caused by them.

Thus the only ionizing agent that reaches the electroscope is the γ rays, and it is found that the observed current, with the magnetic field, is that corresponding to only the last portion of the above curve. We are thus able to detect the presence of γ rays with an absorption coefficient in aluminium of $\mu = 0.11$ and β rays with coefficients $\mu = 12.4$, 42.8, and 390 per centimeter. Not much physical significance can be attached to these latter values, but an estimate of the wave length of the γ rays can be found from the absorption coefficient. Since the density of aluminium is 2.7, its atomic weight being 27 and atomic number 13, we find the absorption coefficient per electron to be

$$\mu_{e\mathrm{Al}} = \frac{\mu M}{\rho N Z} = \frac{0.11 \times 27}{2.7 \times 6.06 \times 10^{23} \times 13} = 1.39 \times 10^{-25}$$

Substituting this in Eq. (10-20) and using the previously cited value for σ_0, we find

$$\lambda_{\mathrm{eff.}} = 0.0128 \times 10^{-8} \text{ cm.}$$

A somewhat more accurate value may be expected if we repeat the experiment using lead for an absorbing material. The observed absorption coefficient for the γ rays in this case is found to be $\mu_{\mathrm{Pb}} = 0.510$. For lead, $\rho = 11.35$, $M = 207$ and $Z = 82$, so that $\mu_{e\mathrm{Pb}} = 1.87 \times 10^{-25}$. Using these values for $\mu_{e\mathrm{Al}}$ and $\mu_{e\mathrm{Pb}}$ in Eq. (10-19), and taking K' equal to 2.2×10^{-2}, as found from the X-ray experiments of the previous chapter, we obtain

$$\lambda_{\mathrm{eff.}} = 0.0157 \times 10^{-8} \text{ cm.}$$

This is in good agreement with the effective mean value, 0.0167 Å, of the harder γ rays as measured by Ellis[1] by the β-ray method, and weighted according to the estimated intensities.

LINEAR ABSORPTION COEFFICIENTS μ OF γ RAYS IN ALUMINIUM PER CENTIMETER
Arranged to show the assumed origin[2]

Element	*M* series	*L* series	*K* series	Nucleus
UX_1	.....	24	0.7	....
UX_2	.....	....	....	0.14
Io	1,088	22.7	0.41	....
Ra	354	16.3	....	0.27
Ra B	230	40	0.57	....
Ra C + C″	.....	....	1.49	0.23, 0.127
Ra D	.....	45	1.17	....
Ra E	.....	....	....	0.24
Ra F	2,700	46	....	....
Rd Ac	.....	25	....	0.19
Ac B	120	31	0.45	.....
Ac C″	.....	....	....	0.198
Ms Th_2	.....	26	....	0.116
Th B	160	32	0.36	.....
Th C″	.....	....	....	0.096

10-18. Experiment on β-ray Spectra.—As a great many of the characteristic β rays have values of Hr less than 3,000 gauss-centimeters, it is possible to build a spectrograph employing a permanent magnet for the field. Since the necessary exposure times occupy several hours this is a great advantage, for it is difficult to maintain the field of an electromagnet constant over long periods. A magnet for precision work has been described by Cockcroft, Ellis, and Kershaw,[3] but a simpler magnet, which is capable of giving very satisfactory results, can be constructed with the aid of ordinary magneto magnets as has been suggested by Dr. Bainbridge. Two slabs of soft iron, such as Armco, about 7 in. long, 4 in. wide, and ½ in. thick act as the pole pieces. To the outsides of these are screwed the magneto magnets. These may be from four to eight in number depending on the strength of the field desired.

The vacuum-tight box fits snugly between these pole pieces. The sides of the box should be soft-iron slabs of the same area as the pole pieces. The thickness of the pole pieces and box sides together should be such that the box width (evacuated region) is about ⅝ in. The edges and bottom of the box may be made from strips of brass $\frac{1}{4}$ in. thick and $\frac{5}{8}$ in. wide. Through one of the sides a brass tube is inserted to permit evacuation. The top of the box, which is about $6\frac{3}{4}$ in. long, $1\frac{1}{2}$ in. wide, and $\frac{1}{4}$ in. thick, is removable and may be waxed in a flanged seat to render the joint between it and the rest of the box vacuum tight. It is convenient for purposes of adjustment to have the source holder, slit, baffles, and photographic plate supported from the top of the box. The source holder may be simply an internally threaded protuberance extending down a few millimeters from the top, about 1 cm. from the inner surface of one end of the box. This holds a screw to the head of which is fastened a stirrup-shaped platinum-wire bow. The straight portion is adjusted parallel to the field and when coated with a radioactive material acts as a line source. About 1 cm. from the source toward the center of the box is a lead block, of width equal to that of the box and 5 or 6 mm. in thickness, which extends down from the top about 0.5 cm. beyond the source. This protects the photographic plate which lies beyond it from any direct β or γ radiation emitted by the source. A lead-jawed slit about 2 mm. wide and of length equal to the box width is situated about 0.5 cm. directly below the source and parallel to it. One jaw is supported by the lead block and the other by a light brass frame extending down from both ends of the top in such a way as to be in contact with the bottom and sides of the box when the top is in position. This frame also supports lead baffles suitably designed so that radiation leaving the source cannot reach the plate by a single scattering process at the walls of the box. The photographic plate on which the β rays are to be recorded is supported in the horizontal plane of the slit by clips on extensions from the top. On the dimensions that have been suggested the plate may be about $\frac{1}{2}$ in. wide and 5 in. long. If a very fine hole is drilled through one of the plate supports, a light may be held over it at the termination of an exposure and a fiducial mark recorded on the plate.

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[1] ELLIS, *Proc. Camb. Phil. Soc.*, **22**, 374 (1924).

[2] Data taken from the Report of the International Radium Standards Commission, *Rev. Mod. Phys.*, **3**, 427 (1931).

[3] COCKCROFT, ELLIS, and KERSHAW, *Proc. Roy. Soc.*, **135**, 628 (1932).

With four large magneto magnets and a box width of $\frac{5}{8}$ in. a field of 350 or 400 gauss may be obtained. The uniformity of the field in the box may be tested with a flip coil and galvanometer, and the absolute value of the field may also be determined in this way. A very convenient method, however, for measuring this field is to suspend a heavy copper-wire frame (in the shape of a U with a flat bottom) in the box from one arm of a balance. A current sent through this frame (contact being made by means of mercury cups in which its bent-over ends are submerged) exerts a force on the balance arm of IlH, where I and H are the current and field strength in electromagnetic units, and l is the length of the bottom of the frame in centimeters. This force may be balanced by weights on the other pan and the magnetic field strength determined to within a fraction of a per cent. This is of the same order as the uniformity of the field that can be obtained throughout the box.

A wire source may be given an exposure of a few hours to thoron or coated with Ra D and mounted in position. The room must then be completely darkened, a plate mounted in position, and the top of the box waxed in place. The box is then evacuated with an oil pump to about 10^{-3} mm. Hg and an exposure of 12 or 15 hr. made. Upon removal of the plate and development, the lines produced by the β rays characteristic of the substance will be observed. The positions of these lines on the plate and the relevant box dimensions are then measured from which the characteristic Hr values can be calculated and the spectrum analyzed in order to determine the γ-ray wave lengths, as has been outlined in Sec. **10-12.** The Hr values are transformed into energy units such as ergs or electron volts, and the characteristic X-ray levels (see Sec. **9-11**) are expressed in the same units. A very convenient table of these is given by Kovarik and McKeehan.[1] The procedure is then to add the observed energies and term values in the proper pairs to determine the energies or wave lengths of the γ rays and incidentally the levels in which conversion of their energies into that of the β rays takes place.

10-19.—Experiment on the Magnetic Deflection of α Particles.—To deflect α particles by magnetic or electric fields is considerably more difficult than a similar type of experiment performed with cathode rays, β particles, or artificially produced positive ions. As is shown by Eq. (4-10), a magnetic field H bends the path of a particle of charge e (e.m.u.), mass m, and velocity v, into a circle of radius r, given by $Hr = mv/e$. The quantity Hr is thus a definite property of any charged particle that has a characteristic velocity and ratio e/m. For the line spectra of β rays, Hr has values ranging from a few hundred up to 5,000 gauss-centimeters, but for α particles this quantity varies from 300,000 to 400,000, so that with 10,000 gauss, the radius of curvature is 30 or 40 cm., and the deflection over a path of a few centimeters is therefore very small.

Unless very active sources, such as Ra C or C′ are available, it is not feasible to measure the deflection of a single narrow beam, owing to the exceedingly small number of particles that reach the recording apparatus every second. Satisfactory results can be obtained, however, with polonium, using an extended source after the manner of Rutherford's original scheme. This is equivalent to a great many line sources parallel to each other, the particles from each passing between closely spaced plates; the critical field strength is observed at which the particles just fail to emerge, the radius of curvature being calculated from the geometry. This method permits the use of weak sources and does not require the apparatus to be evacuated.

The essential part of the device is the system of parallel plates, which must be designed to suit the auxiliary apparatus available. Consider first a pair of plates of length L and width W, separated by a very small distance x, a magnetic field being applied parallel to the width coordinate as in Fig. 10-6. Those particles that start directly down the channel are deflected toward one plate in a circular path and, if the field is sufficiently strong, will be unable to emerge and enter the ionization chamber of an electroscope directly below. Other particles, however, which left the source at an angle, will still be able to escape, and the last to be intercepted as the field is increased are those that leave the source at C, just graze the opposite plate at its mid-point A, and emerge as shown. In the triangles ABC and BCD, whose bases form the diameter of the circular path of radius r, we have the relation

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[1] Kovarik and McKeehan, *Bull. Nat. Research Council*, **10**, 98 (1925).

$$\frac{x}{L/2} = \frac{L/2}{2r - x} \cong \frac{L/2}{2r}$$

since in practice x is negligible compared to $2r$. Hence

$$r = \frac{L^2}{8x}$$

As Hr is a constant for a given type of α particle, and as there is usually a maximum value to the available field, we desire to have this critical radius as large as possible. The length L must be somewhat less than the range of the particles used, as part of this range must fall within the ionization chamber; furthermore, there is generally a little wasted space between the slit system and the electroscope. Therefore x must be small.

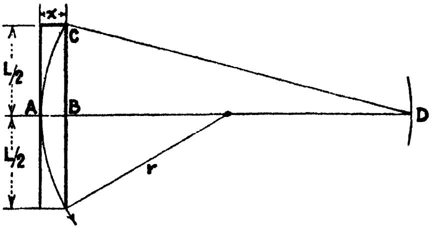

FIG. 10-6.—A diagram of the magnetic deflection of α particles. The magnetic field is perpendicular to the plane of the paper.

With sources of no great activity such as polonium, the total intensity must be made as large as possible. This is effected by increasing the width W of the plates up to the point at which the separation of the pole pieces of the magnet limits the field to the critical value and by increasing the number of parallel plates. This factor, however, cannot be extended indefinitely for it is limited by the size of the pole pieces available.

A compromise design that has been used successfully is the following. The plates are of mica, 0.013 cm. thick, 2.5 cm. long, and 0.8 cm. wide. One hundred and one of these are piled together, with somewhat longer and narrower mica strips alternating between them, each 0.01 cm. thick. The pile is held together by a coating of wax along the two sides, and the narrow spacing strips are then withdrawn, leaving 100 parallel channels each 0.01 cm. in width. The whole set-up is thus a rectangular prism, 2.5 cm. long, a little over 1 cm. wide, and about 2 cm. thick. The source is a silver plate, 2 by 1 cm., that has been stirred in the hydrochloric acid solution of crushed radon tubes for about 1 hr. This is waxed over one end, and the whole α-particle "gun" is waxed to one of the pole pieces of the magnet, so that the particles are sent downward. The electroscope is mounted beneath, with the entrance gauze of the ionization chamber within about 4 mm. of the slit system. This gap permits the introduction of a thick sheet of mica or aluminium for the purpose of obtaining the natural leak of the instrument. It is worth while redetermining this quantity at intervals throughout the experiment, particularly when fields near the critical cut-off value are used, for then the observed activity does not differ greatly from the leak itself and a small change would cause serious errors in the net activity. The field strength is determined with a bismuth spiral or a search coil and calibrated fluxmeter.

A typical curve is shown in Fig. 10-7, wherein the critical field appears to be 3,850 gauss. With $L = 2.5$ cm. and $x = 0.01$ cm., r has the value 78 cm., so that $Hr = Mv/E = 3.0 \times 10^5$. This is of the proper order of magnitude for the Hr value of polonium α particles. Greater accuracy cannot be expected as the velocity is not constant but decreases along the path.

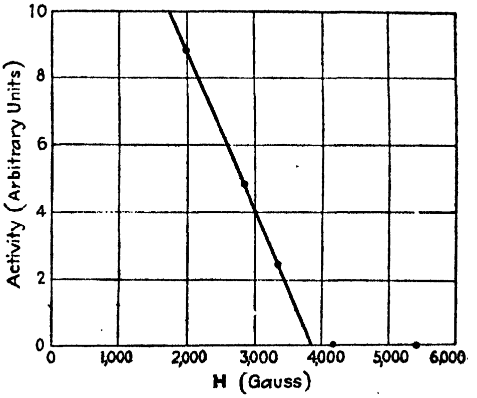

FIG. 10-7.—The variation of the ionization current with increasing magnetic field, in the deflection experiment with α particles.

A brief calculation will indicate the difficulties of determining with any accuracy the deflection of an α particle in an electric field. If the particle travels a distance L between two plates x cm. apart, the lateral force and acceleration a are given by

$$\frac{10^8 V}{x} E = Ma$$

where E is the charge and $10^8 V/x$ is the field strength in electromagnetic units per centimeter, V being in volts. If the particles are deflected an amount x in the distance L, we have $x = \frac{1}{2}at^2$, where t is the time of flight between the plates, or $t = L/v$. Hence

$$\frac{10^8 V}{x} E = M\frac{2x}{t^2} = \frac{2Mxv^2}{L^2}$$

or

$$\frac{10^8 VL^2}{2x^2} = \frac{M}{E}v^2$$

The velocity of α particles from polonium is $v = 1.59 \times 10^9$ and $E/M = 4{,}823$, so that the right side of this equation is 5.24×10^{14}, or $VL^2/x^2 = 1.048 \times 10^7$. As the maximum practical value for L is about 3 cm., with a polonium source, even of considerable extent, this means x must be of the order of 0.03 cm. with 1,000 volts. Excellent insulation and a high vacuum would be necessary to prevent sparking at this gradient.

10-20. Geiger-Müller Counters.—The counting of α particles and the measurement of their ranges can be done by means of the so-called Geiger-Müller counter.[1] The essential part of this instrument is a fine wire or point which is raised to a high potential. When ions are produced in the region of influence of this electrode, as by the passage of an α particle, they are acted on by the intense field and produce more ions by collision. As a result of this cumulative process, the number of ions is multiplied many fold and the current to the electrode is large enough so that it may be detected directly with an electrometer or may be amplified to operate a loud speaker or counting relay. The entrance of an α particle into the counter sets it off as by a trigger action, and the discharge continues until the potential difference has dropped below a critical value. An interesting account of the design and operation of counters has been given by Emeleus,[2] but the exact mechanism of operation in the presence of various stimuli, such as α and β particles and γ rays, is not completely understood and the methods of use are largely empirical. Recently, for α-particle counting and range measurement, ionization chambers rather than counters have been used. The current, due to the ions produced directly by the α particle, is measured without the use of the cumulative counter action. This technique,[3] which constitutes a great advance in radioactive measurements, employs chambers with plane electrodes and special rapid automatic counting circuits.

In the counters, as originally used by Rutherford and Geiger,[4] the current to the electrode was measured directly with an electrometer. This method, however, is inconvenient and cumbersome. Instead, the current through the counter may be used to alter the potential of the grid of a vacuum tube and the resulting change in plate current may be detected with a coarser instrument or further amplified to operate a loud speaker or automatic counting device.

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[1] Geiger and Müller, *Physik. Zeits.*, **29**, 839 (1928); **30**, 489 (1929).

[2] Emeleus, *Proc. Camb. Phil. Soc.*, **22**, 676 (1925).

[3] Fränz, *Zeits. Physik*, **63**, 370 (1930).
Greinacher, *Zeits. Physik*, **36**, 364 (1926); **44**, 319 (1927).
Ward, Wynn-Williams, and Cave, *Proc. Roy. Soc.*, **125**, 713 (1929).
Rutherford, Ward, and Wynn-Williams, *Proc. Roy. Soc.*, **129**, 211 (1930).
Wynn-Williams and Ward, *Proc. Roy. Soc.*, **131**, 391 (1931).
Wynn-Williams, *Proc. Roy. Soc.*, **132**, 295 (1931); **136**, 312 (1932).

[4] Rutherford and Geiger, *Proc. Roy. Soc.*, **81**, 141 (1908).
Rutherford and Geiger, *Phil. Mag.*, **24**, 618 (1912).

A circuit which may be used for the detection of various types of radiation is shown in Fig. 10-8. The counter itself is composed of a brass tube about 2 cm. in diameter and 5 or 6 cm. long with a copper wire 0.05 cm. in diameter supported along its axis by insulating plugs. When used for α particles the window W should be very thin and of some light material such as mica, cellophane, or aluminium. If the counter is used to detect β particles, the window may be much thicker, or, if it is used for γ radiation, the window may be dispensed with altogether. The construction of the counter is not critical unless a very rapid rate of counting is desired, in which case the capacity must be kept as low as possible. The action of a poor counter is erratic, but the occasional good one is very reliable. The optimum working conditions must be found by trial and error for any particular one. Almost any counter will operate at atmospheric pressure, but more satisfactory results can frequently be obtained if it is evacuated to about 5 or 10 cm. Hg. The range of operating potentials over which the counter will yield a true record of the ionizing agency depends on what it is that is being counted, the pressure, and the chamber design. The counter is easiest to use with α particles and a large potential range (above the critical value where action commences) generally exists throughout which an accurate count of the number is obtained. At atmospheric pressures potentials of from 1,500 to 2,500 volts are generally satisfactory, while at lower pressures potentials of a few hundred volts frequently suffice.

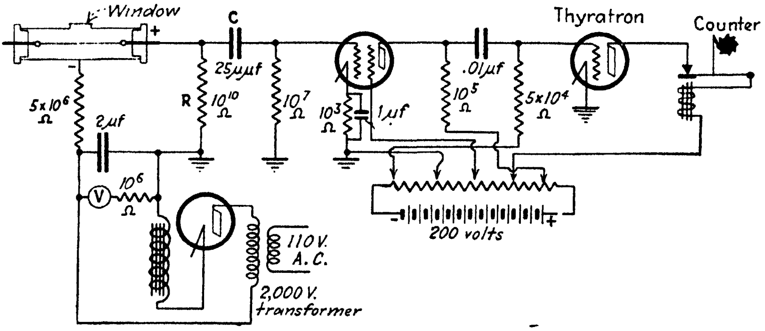

FIG. 10-8.—A Geiger-Müller counter circuit and amplifier.

The operating potential may be supplied conveniently by a small 2,000-volt transformer which charges a condenser of about 2-μf. capacity through a kenotron and choke coil. The potential may be measured with an electrostatic or high-resistance voltmeter and adjusted by means of a rheostat in the primary circuit of the transformer. The negative terminal of the condenser is connected through a resistance of about 5 megohms to the outer cylinder of the counter. A high leakage resistance R of about 10^{10} ohms connects the central electrode to the ground, and sudden changes in the potential of this electrode affect the grid of the screen-grid tube through a small condenser c of from 10- to 50-$\mu\mu$f. capacity. The rest of the circuit is simply a resistance-coupled amplifier. This should contain two or three stages if a loud-speaker or automatic counter is to be used. For best results the leads from the counter and the amplifying system should be electrostatically shielded. A more detailed description of this type of counting system and its characteristics has been given by Van den Akker.[1] Difficulties in operation due to fluctuations in voltage of the main power lines may be avoided to a large extent by incorporating a simple vacuum-tube voltage stabilizer into the kenotron circuit. Details of such stabilizing circuits have been given by Johnson and Street.[2]

Such a counter may be used instead of a fluorescent screen or electroscope to measure α-particle ranges. The technique of this measurement, using a counter as the detecting instrument, is the same as that described in the preceding section except that the counter window replaces the fluorescent screen. As the source is advanced toward the counter, a critical distance is reached at which impulses are recorded. The number of counts, then, increases in proportion to the increase in solid angle. The correction for the thickness of the window may be made by taking a second run with an additional film interposed of the same stopping power as the window.

10-21. Experiments on Growth and Decay. Sources.—The difficulty of obtaining radioactive preparations at a moderate cost is one of the limiting factors in the performance of many interesting experiments that require great activity. The number of particles expelled per second is given by the product of the number of atoms of the substance times its disintegration constant, so that materials with a very short period are desirable. For this reason, Ra C′ has been used extensively in the determinations of the charge, value of E/M, and number of α particles per second, etc., since its λ equals 10^6 sec.$^{-1}$, with consequent intense activity. The various radium products are generally obtained from the radon liberated by several grams of radium. Such a procedure is obviously limited in its general use.

Radon in limited quantities can, however, be obtained from carontite, which is not so difficult to procure and which contains about 2 per cent of U_3O_8. A quantity of this is crushed, mixed with an equal amount of sodium acid phosphate, and sealed in a glass tube. Practically the equilibrium amount of radon accumulates within several weeks and may be driven from the mineral by heating the tube with a Bunsen flame. One end of the tube is connected with rubber pressure hose through a stopcock to the ionization cylinder mounted over the electroscope. The cylinder is evacuated from its other orifice, which is then closed with another stopcock. After several minutes' application of the flame, the tip of the glass tube within the rubber hose is broken, and then the other end, so that the radon is sucked into the cylinder and isolated by closing the valves. After 4 or 5 hr., the resulting products come into equilibrium with the radon and, thereafter, decay at the rate of the radon itself. After this interval, therefore, the ionization current (I) is directly proportional to the number of radon disintegrations per second and hence to the number of these parent atoms present. We may rewrite Eq. (10-2) as

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[1] VAN DEN AKKER, *Rev. Sci. Inst.*, **1**, 672 (1930).

[2] JOHNSON and STREET, *J. Franklin Inst.*, **214**, 155 (1932).

$$I = I_0 e^{-\lambda t}$$

so that

$$\log_e I = \log_e I_0 - \lambda t$$

and a plot of $\log_e I$ against the time will give a straight line of slope $-\lambda$, the disintegration constant of radon. (As usual, log to the base 10 may be used, and the resulting slope multiplied by 2.303.) The half-life is then determinable through the relation $T = 0.693/\lambda$ [Eq. (10-3)].

Great care should be taken to keep the radon from escaping into the room as it would contaminate that region of the laboratory and render it unfit for any ionization measurements.

The half-period of *thoron* may be determined in a similar manner. Thorium hydroxide or carbonate is placed in a glass tube, the ends of which are closed by stopcocks, one of them communicating with the ionization chamber. The equilibrium quantity of thoron is reached in less than an hour. The glass tube is heated and the thoron admitted to the previously evacuated chamber, as in the experiment with radon. Due to the short half-life of thoron (54.5 sec.) it is generally necessary to observe the intervals for the electroscope leaf to pass over successive divisions across the entire scale. The correction for non-uniformity of speed is found by observing the times of fall over corresponding divisions when a constant ionizing source, such as polonium, is present.

The products of thoron are safe and convenient to work with, as there is no long-lived product in the disintegration chain beyond mesothorium. There is thus little danger of permanent contamination of the laboratory. The parent substance, radiothorium, may usually be obtained from the gas-mantle industry since it grows from mesothorium which is a by-product in the commercial production of thorium. The radiothorium preparation may be placed in a shallow brass tray in a lead-shielded container, as shown in Fig. 10-9. This chamber should be as gas-tight as possible to prevent the diffusion of thoron. A brass electrode which passes into the chamber through an insulating plug supports the plate or wire which is to collect the decay products; a convenient arrangement is to have the electrode threaded to take a small standard screw. A platinum wire with a bead on the end is brazed to the screw head and all except the bead is covered with an insulating and heat-resisting compound such as glyptal lacquer. The bead may be made by inserting the end of the wire in an oxygen flame and allowing the drop of platinum to grow to the desired size. The source is screwed into the electrode and removed, after deposition of the active material, with tweezers that are reserved for this purpose.

The electrode is charged 100 or 200 volts negatively with respect to the container, a resistance such as one or two incandescent lamps being placed in the circuit to guard against accidental short circuits. In this manner the decay products of thoron are collected on the bead by the so-called *recoil method.* It appears that during the process of disintegration, an atom loses temporarily one or more of its extranuclear electrons and hence is positively charged, so that during the recoil of the explosion, it is drawn to the negatively charged surface. The immediate product, Th A, has a half period of 0.1 sec., so that what practically is deposited is Th B, with $T = 10.6$ hr. If the source is given a short exposure of this sort, say 5 or 10 min., and then placed over an electroscope, the subsequent transformations may be followed. Disintegration of Th B is accompanied by β rays, whose ionizing power is very weak, whereas an intense current is produced by the α rays from Th C. Consequently, the α activity increases as Th C is developed, reaching a maximum in

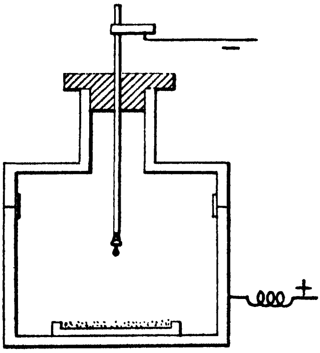

FIG. 10-9.—An apparatus for collecting thorium active deposit by the recoil method.

$$t_{\max} = \frac{2.303}{1.91 \times 10^{-4} - 1.82 \times 10^{-5}} \log_{10} \frac{1.91 \times 10^{-4}}{1.82 \times 10^{-5}} = 1.358 \times 10^{4} \text{ sec.} = 3.77 \text{ hr.}$$

Equilibrium is reached at that time, since the half-life of Th C (60.5 min.) is less than that of the parent, and the subsequent activity dies down at the rate of Th B. From this latter part of the curve, as shown in Fig. 10-10, the disintegration constant of Th B may be found. If the exposure to the thoron is prolonged to several hours, the Th C grows to practically its equilibrium value on the bead before it is removed, and the activity, when tested, shows at once the decay characteristic of the long-lived parent Th B.

A bead that has received such a long exposure can be cleansed of Th B by heating it for a short time to a red heat so that Th C alone is left on it, and its half-life may be determined from the fall in activity. An alternative procedure is to dissolve off the Th B and C from a bead that has had a long exposure by placing it in concentrated hydrochloric acid. This is then diluted, and Th C will be deposited on a nickel plate that is placed in the solution.

Polonium (Ra F) is the most convenient source of α particles (if large quantities of radon are not available from which to derive Ra C and C′), and it has the advantage of breaking up at a sensibly constant rate. A few old radon tubes or "needles" can usually be obtained from hospitals; these are crushed in a mortar and put in a half-normal hydrochloric acid solution. Radon has a half-life of 3.8 days, so that in 5 weeks after the tubes are filled, all but about 0.1 per cent of this gas has decayed. The products Ra A, B, C, C′, C″ have half-periods all less than 27 min., so that they very shortly come to equilibrium and decay with the longer period of Rn. In 5 weeks, therefore, well over 99 per cent of the material is Ra D, whose half-life is 22 years. This changes slowly, with the emission of β rays, to Ra E, for which $T = 5.0$ days. This therefore comes to equilibrium with Ra D in 53 days [see Eq. (10-9)] and thereafter decays with the emission of β particles at the slow period of Ra D, changing to form Ra F or polonium, whose half-life is 140 days. This breaks down to form lead, accompanied by α particles of considerable energy. This α emission reaches a maximum value in a little over 2 years, after which it decreases at the slow rate of Ra D. Polonium may be obtained from the hydrochloric acid solution by stirring a silver plate in it for some minutes; the polonium precipitates upon the metal. Such a source of isolated Ra F loses its activity with a half-life of 140 days, so that the α emission is essentially constant for all experiments that take only a few hours to perform.

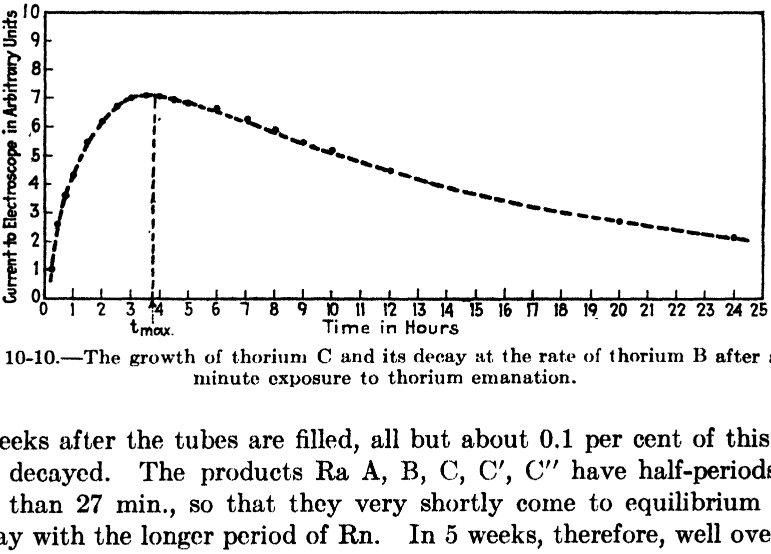

FIG. 10-10.—The growth of thorium C and its decay at the rate of thorium B after a 15-minute exposure to thorium emanation.

Further details on the preparation of sources may be found in the works of Rutherford, Chadwick, and Ellis,[1] Hevesy and Paneth,[2] Soddy[3] and Makower and Geiger.[4]

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[1] RUTHERFORD, CHADWICK, and ELLIS, "Radiations from Radioactive Substances," Macmillan (1930).

[2] HEVESY and PANETH, "Radioactivity," Oxford University Press (1926).

[3] SODDY, "The Chemistry of the Radio-Elements," Longmans (1914).

[4] MAKOWER and GEIGER, "Practical Measurements in Radioactivity," Longmans (1912).

APPENDIX A

INSTRUMENTS FOR MEASURING SMALL CURRENTS AND POTENTIAL DIFFERENCES

Moving-coil, or D'Arsonval, Galvanometers.—In these instruments a light rectangular coil of wire, carrying a mirror for the reflection of a light beam, is suspended by a fine wire so that it is free to rotate between the poles of a permanent magnet. A solid steel cylinder, coaxial with the suspension, occupies the central region between the pole pieces as shown in Fig. A-1. As a consequence the magnetic field is nearly radial over the region through which the coil moves. A current flowing in along the suspension and out along the weak spiral wire at the bottom causes a torque which produces a displacement of the light beam reflected from the mirror. If the magnetic flux density in the gap is B, and n is the number of turns, and a and b are the length and diameter of the coil, respectively, the torque for a current i is given by

$$T = nabBi$$

In equilibrium this is balanced by the restoring couple of the suspension which may be taken as proportional to the angular displacement θ, the constant of proportionality being k'.

$$k'\theta = nabBi$$

If the beam of light is reflected back to a straight scale at a distance D, its deflection d from the zero position when the light falls normally on the scale is given by

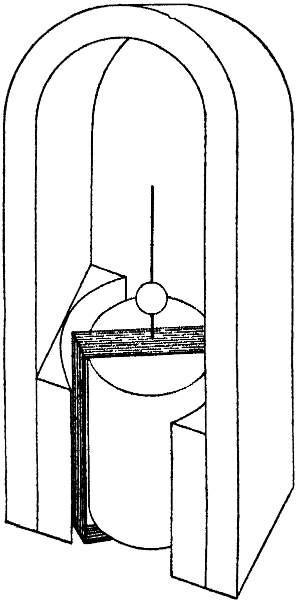

FIG. A-1.—A moving-coil galvanometer.

$$d = D \tan 2\theta$$
$$\cong \frac{2DnabB}{k'} i$$

if 2θ is small. The tangent correction, in general, approximately cancels the effect of the non-radial nature of the field, so that d is directly proportional to i, the constant of proportionality appearing explicitly above. For very accurate work, however, the galvanometer scale must be calibrated over its entire length. The proportionality factor determines the sensitivity of the galvanometer, which it is seen may be increased by increasing the terms in the numerator or by decreasing the restoring torque of the fiber. For convenience in operation the period of oscillation of the coil cannot be unduly long. This imposes a further condition which limits the practical sensitivity.

Current Sensitivity.—The so-called *figure of merit* is defined as the current in amperes through the coil necessary to produce a displacement of the light beam of 1 mm. at a distance of 1 meter. This varies from 10^{-7} to 10^{-11} amp. for standard galvanometers. For greater currents pointer instruments may be used and for smaller ones an electrometer is required.

Voltage Sensitivity.—Two definitions are in use for this quantity. The microvolt sensitivity is defined as either (1) the potential in microvolts which must be applied to the galvanometer terminals to produce a deflection of 1 mm. at 1 meter, or (2) the potential in microvolts which must be present in the series circuit containing the external critical damping resistance to produce a deflection of 1 mm. at 1 meter This latter definition, through which the voltage sensitivity depends on the current sensitivity, the galvanometer resistance R_g, and the external critical damping resistance R_c, is most common in this country. This sensitivity varies from 10^{-5} to 5×10^{-8} volt for standard galvanometers. A galvanometer is the most accurate instrument available for the measurement of small potential differences.

The equation of motion of a galvanometer coil is

$$I\frac{d^2\theta}{dt^2} + F\frac{d\theta}{dt} + k'\theta = G$$

where I = moment of inertia of the coil.

F = damping constant. This is the sum of the air and fiber damping f and the electromagnetic damping which is proportional to the induced current or inversely proportional to the total resistance of the circuit. $F = f + q/R$.

G = couple due to the potential applied to the galvanometer terminals.

Neglecting G, which merely displaces the zero position, the equation is seen to be the familiar one of damped simple harmonic motion. The critically damped condition, in which it is most convenient to work, is given by

$$F^2 = 4Ik'$$

As f is generally negligible and $q = (nabB)^2$, we have

$$R_c = \frac{(nabB)^2}{2\sqrt{k'I}} - R_g$$

This expression shows how the critical damping resistance is related to the galvanometer constants. Its value is generally supplied by the galvanometer manufacturer, or it may be determined experimentally. When the resistance of the external circuit with which the galvanometer is to be used is quite small, as in the case of a thermocouple, the galvanometer should be of the high voltage-sensitivity type with an external critical damping resistance approximately equal to that of the thermocouple for most efficient operation. When the external circuit resistance is large, as in the case of a photoelectric cell, a high current-sensitivity instrument should be used with the critical damping resistance shunted across its terminals.

A galvanometer may be calibrated so that the observed displacements may be converted directly into amperes flowing through the coil by the arrangement shown in Fig. A-2. A battery whose potential is measured by the voltmeter V is placed in the circuit containing the galvanometer, a shunt R_2, and a series resistance R_1, by means of a reversing switch. If i_g is the current through the galvanometer and i is the current through R_1, we have

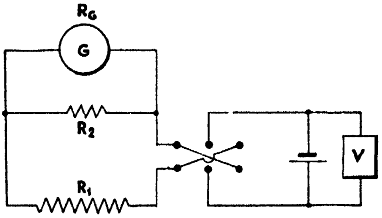

FIG. A-2.—The circuit for calibrating a galvanometer.

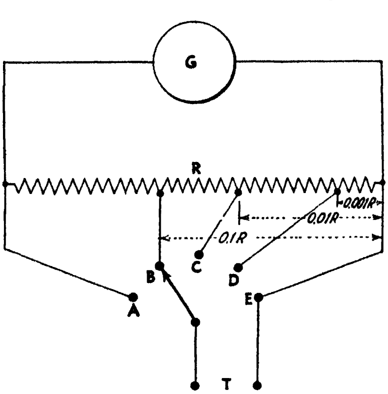

FIG. A-3.—An Ayrton shunt.

$$iR_1 + i_g R_g = V$$

and

$$i_g R_g = (i - i_g)R_2$$

or

$$i_g = \frac{R_2 V}{R_1R_2 + R_1R_g + R_2R_g} = kd$$

from which the proportionality constant k between i_g and the displacement d can be determined if the potential and resistances are known. In practice the potential V may be obtained from a storage battery, R_1 may be a resistance of about 10^6 ohms, and R_2 is given a series of values from 1 to 10 ohms; an average value of k is calculated from the displacements observed on reversing the switch.

The most convenient method of reducing the galvanometer sensitivity is by the use of an Ayrton shunt, as shown in Fig. A-3. A resistance R, approximately the external critical damping resistance of the galvanometer, is shunted across it, and taps from this resistance such that $EB = 0.1R$, $EC = 0.01R$, and $ED = 0.001R$ lead to the dial switch. If i is the current at the terminals T and the switch is set so that the effective shunt resistance is R/n and the resistance in series with the galvanometer is $R - \frac{R}{n}$, we have for the current through the galvanometer

$$i_g = \frac{i}{n} \frac{R}{R + R_g}$$

Thus the taps B, C, and D reduce the deflection in the ratios 0.1, 0.01, and 0.001, respectively, provided that the external resistance is so large that i is unchanged when the position of the switch is altered; if this is not so, a correction must be applied. If R is much larger than R_g, little sensitivity is lost in the A position.

In working with a high-sensitivity galvanometer, precautions such as those for electrometer work should be taken. All wiring should be of copper and junctions should be made with solder using a non-corrosive flux such as rosin. Glass, hard rubber, or bakelite insulation is satisfactory, and if possible one terminal of the galvanometer should be grounded. Zero shifts which are not due to imperfections in the galvanometer itself generally arise from faulty insulation, thermoelectric effects, or local action at badly made contacts.

Electrometer-type Instruments.—In principle these instruments are for potential measurement, and their current sensitivity arises from the very high shunt resistance when used for constant deflections or from their small capacities when a rate of deflection method is employed. Except in the case of the electrometer tube, which is strictly an amplifier, the moving element is actuated by electrostatic forces, and from the potential difference which is directly measured the current flowing to the instrument is inferred. This type of instrument is capable of greater sensitivity than the electromagnetic type when the external circuit resistance is large.

Many different electrometer designs have been suggested and each has its own peculiar advantages. The so-called string electrometer,[1] which is similar to an electroscope in operation, employs a very light quartz fiber as the moving element, and its displacement under electrostatic forces is observed with a microscope. These instruments have, in general, small voltage sensitivities, of the order of 10^2 divisions per volt, but they also have small capacities and short periods and are very stable and convenient in operation. The external-circuit technique is similar to that which will be described in connection with the quadrant electrometer.

The other general type of electrometer employs as its moving element a light needle capable of rotating on a fine suspension between the two electrodes whose potential difference is to be measured. The deflection of the needle is observed, as in the case of the galvanometer, by the displacement of a spot of light reflected from a small mirror attached to the moving system. The simplest of these electrometers, namely, the Dolezalek type, which is suitable for the measurements indicated in the text, has a voltage sensitivity of from 10^2 to 5×10^3 mm. per volt at 1 meter, depending on the design of the instrument, the restoring torque of the fiber, and the potential applied to the needle. More sensitive instruments operating on the same principle have been designed by Compton[1] and Hoffmann.[2] The vacuum instrument designed by the latter may be operated stably at a sensitivity of 3×10^4 mm. per volt at 1 meter. The capacity is so small and the stability so great that currents of the order of 10^{-19} amp. may be detected using a rate of deflection method. This is approximately one electron per second. Largely due to its stability, it is the most sensitive current-measuring instrument which has been devised.

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[1] Wulf, *Physik. Zeits.*, **15**, 250, 611 (1914); **26**, 352 (1925).

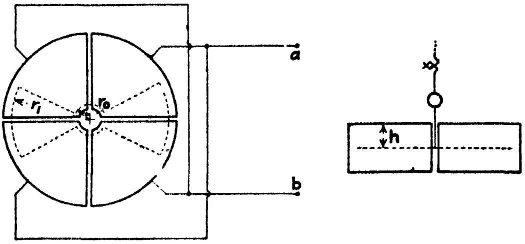

FIG. A-4.—The quadrant electrometer.

In the Dolezalek electrometer a light aluminium or sputtered mica needle with radial edges is suspended in a shallow cylindrical brass box divided into four insulated quadrants. Opposite pairs of these are connected together, and it is the potential difference between these pairs that is measured by the deflection of the needle. The needle itself is waxed (the joint being conducting) to a light wire carrying the mirror which is in turn attached with a small hook to a fine sputtered quartz fiber suspended from a knurled head at the top of the instrument. The whole is enclosed in a metal case. The action of the instrument may be analyzed as follows. Consider the needle and one pair of quadrants as forming a plane condenser. If S_a is the area of the needle under the quadrants a, the capacity is $2S_a/4\pi h$, where h is the distance from the needle to the top or bottom of the quadrants. If the potential of the needle is V_n and that of a is V_a, the energy in the condenser, $CV^2/2$, is $\frac{S_a(V_a - V_n)^2}{4\pi h}$. If the total area of the needle is S, the total energy, considering the condensers made up of both pairs of quadrants and the needle, is

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[1] COMPTON, A. H. and K. T., *Phys. Rev.*, **14**, 85 (1919).

[2] HOFFMANN, *Physik. Zeits.*, **13**, 480, 1029 (1912); **15**, 360 (1914); **25**, 6 (1924); *Schriften d. Königsberger Gelehr.-Gesell.*, **4**, 1 (1927).

$$E = \frac{QV}{2} = \frac{S_a(V_a - V_n)^2}{4\pi h} + \frac{(S - S_a)(V_b - V_n)^2}{4\pi h}$$

The torque on the needle is, by definition, the negative derivative of E with respect to θ, the angle variable. Considering everything constant but S_a, we have

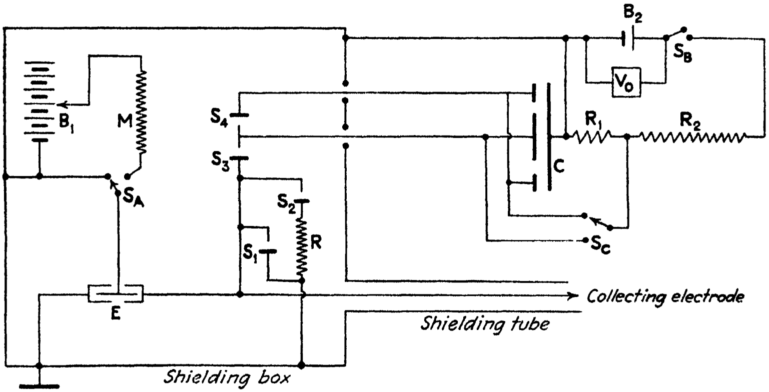
$$T = -\frac{(V_a - V_n)^2 - (V_b - V_n)^2}{4\pi h}(r_1^2 - r_0^2)$$

since $dS_a/d\theta = r_1^2 - r_0^2$. In equilibrium this is balanced by the restoring torque of the fiber which may be taken as proportional to the displacement from the equilibrium position, *i.e.*, as $k'\theta$. Since $V_a + V_b$ is in general very small in comparison with $2V_n$, we may write the final expression after equating T and $k'\theta$ as

$$\theta = \frac{(r_1^2 - r_0^2)}{2\pi k'h}V_n(V_a - V_b)$$

Thus to this approximation we see that the deflection θ is proportional to $(V_a - V_b)$, and hence a linear relation exists between the potential difference between the quadrants and the deflection of the needle. This is not strictly true, however, and, as the actual displacement of the light spot introduces a further non-linearity, the scale must be calibrated for accurate work. It is seen from the above relation that V_n should be large and k' small for the maximum sensitivity. The former can be increased up to 200 or 300 volts, which is as large a needle potential as can be used with stability in the average instrument. The constant k' is determined by the quartz fiber, and when a very fine one is used the period is extremely long. Any considerable increase in $r_1^2 - r_0^2$ or decrease in h increases the capacity of the instrument, which is inadvisable.

The instrument is mounted in a large grounded metal box with room for the necessary switches and testing equipment. The front of the box has a glass window for the admission of the light beam and the side should swing completely open for adjustment. If the box is fairly tight, a drying agent such as $CaCl_2$ or P_2O_5 in a container may be placed inside it with advantage, particularly in damp climates. The greatest difficulty with electrometer work is generally caused by imperfect insulation, often due to films of moisture. The electrometer is set up with the mirror facing the window and the needle lying symmetrically between the quadrants, as shown in Fig. A-4. With both quadrants grounded, a small potential (5 or 10 volts) is placed on the needle by the battery B_1 of Fig. A-5. This is conveniently made from several B-battery units connected in series with a protective resistance M of about 10^6 ohms. A grid leak is satisfactory as it is merely to protect the needle and suspension in case of accidental contact with the quadrants. In general the equilibrium position of the needle will change when it is grounded or raised to a small potential by the switch S_A. This may be corrected by making small changes in the level of the instrument as a whole and slightly altering the height of the needle between the quadrants if necessary. When this adjustment has been properly made, the zero position of the needle is the same for either position of switch S_A, and the full potential of B_1, which may be from 100 to 300 volts, may then be applied.

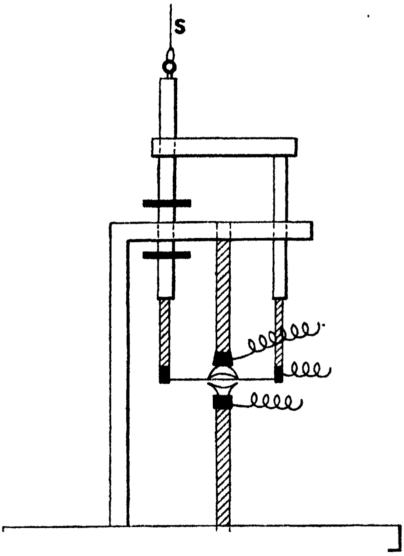


B_1, 200-volt battery
M, Grid leak ($10^6 \Omega$)
R, High resistance (10^8 to $10^{11} \Omega$)
C, Calibrating condenser
E, Electrometer

S_1 to S_4, Highly insulated switches
B_2, Calibrating battery
V_0, Voltmeter
R_1, Variable low resistance
R_2, High resistance ($10^4 \Omega$)

FIG. A-5.—A diagram of electrometer connections.

Figure A-5 illustrates a convenient arrangement for the calibration and use of an electrometer. B_2, (which is a calibrating battery of a few volts whose potential is measured by the meter V_0), R_2 (a fixed resistance of several thousand ohms), and R_1 (which may be a resistance box, variable from 1 to 100 ohms) form effectively a potentiometer circuit. The common contact of these resistances leads to the switch S_c; the pole of this switch connected to the central element of the condenser C should be highly insulated. This condenser, which is used for calibration including the measurement of the high resistances used at R, should have a well-insulated central element. Such a guard-ring condenser with a capacity of about 50 cm. ($\sim 50 \mu\mu$f.) may be purchased, or it may be made in the following way. A smooth brass tube about 25 cm. long and 3 cm. in internal diameter is mounted horizontally on a wood or metal base. This forms the outer grounded electrode. A second brass tube 15 cm. long and 3 or 4 mm. smaller in external diameter is mounted coaxially on a glass rod by means of quartz spokes waxed in place at either end. A wire soldered to it internally leads out along the glass rod. Two shorter pieces of the same tube, about 5 cm. long, are also mounted coaxially on the glass rod with bakelite plugs or glass spokes a few millimeters from the central element. These are connected together, also internally, and constitute the guard ring. The glass rod carrying the three tubes is then inserted in the outer tube and supported at its ends in such a way that the cylinders are coaxial and the clearance uniform around the circumference. The capacity may be calculated from the equation for a cylindrical condenser in Chap. I. $C = \dfrac{L}{\left(2 \log_e \dfrac{b}{a}\right)}$, where L is the length of the central element and b and a are the external and internal diameters of the dielectric layer, respectively. All insulation of the central element and its connections should be of amber or quartz if possible. Pyrex cane can be used if quartz is not available.



Quartz insulation is hatched; S is the control string.

FIG. A-6.—Detail of the electrometer switch $S_{3,4}$.

The switches S_1 to S_4, which are highly insulated, are placed inside the box and operated by suitably guided threads or strings from the observer's seat in front of the scale. There are many alternative methods of switch construction, the essentials being high insulation and clean and positive contacts with as few joints between different metals as possible. Difficulties with zero adjustments or drifts are generally due to dirty contacts or faulty insulation. As with all connections the soldering should be done with a non-corrosive flux such as rosin, and the joints should be kept as small and clean as possible. A convenient and satisfactory design for $S_{3,4}$ is shown in Fig. A-6. The simplification for S_1 and S_2 is obvious. A brass angle carries a brass frame, operated by gravity and the string S, which can slide up and down a few millimeters between stops. This carries quartz rods, waxed into holes, which in turn have a platinum wire, wrapped and waxed in place, stretched across their free ends. At the two extreme positions of the switch this wire strikes the platinum wire bows wrapped and waxed to the quartz rods mounted vertically in the brass angle and base plate. The connections from the platinum contacts are as indicated in Fig. A-5. The internal wiring should be supported at as few places as possible; where these additional supports are necessary they should be of quartz. Ground connections may be made to the inside of the shielding box. The lead to the collecting electrode, whose potential is to be measured, runs through a grounded brass or galvanized tube 3 or 4 cm. in diameter. This may be jointed at intervals. The insulated supports necessary at suitable distances and at angles may be conveniently made with quartz rods waxed into holes drilled opposite one another in the sides of the shielding tube. The wire passing through the tube is quite small (No. 36 is satisfactory), so that the lead capacity is small. It may be fastened to the centers of the quartz insulators with a drop of wax.

The high resistances used at R are of the order of several thousand megohms. They are supported on insulators; one end is grounded and the other leads to the switch S_2. Such resistances may be purchased or they may be constructed in various ways. Probably the most satisfactory ones are made by sputtering or evaporating a thin metal or carbon film on a glass rod in an evacuated tube.[1] India-ink lines[2] ruled on a good grade of typewriter paper are adequate for most purposes. They may be carefully dried and sealed in glass tubes, the terminals being connected to electrodes sealed through the ends, or they may be threaded through a U-tube which is then filled with melted paraffin. In either case the values of the resistances change with time and they must be calibrated occasionally.

The potential calibration may be made by closing S_b, connecting S_c to the center pole of $S_{3,4}$ and closing S_3. The deflection observed when S_1 is opened corresponds to a potential between the quadrants of $V_0R_1/(R_1 + R_2)$. By varying R_1 throughout a convenient range, the scale may be calibrated. A graph of the quadrant potential as a function of the deflection is plotted for subsequent reference.

To obtain the capacity of the electrometer and its connections, the following procedure may be adopted. S_c is connected to the guard rings of the condenser, S_4 is closed, and S_1 and S_2 are opened. In this way the condenser is charged to a potential $V_0R_1/(R_1 + R_2)$ and the electrometer is uncharged. S_4 is then opened and S_3 closed, which causes the charge of C to be shared with the electrometer system of capacity C_e; the resulting potential V' is obtained from the electrometer deflection. We thus have

$$Q = \frac{V_0 R_1}{R_1 + R_2} C = (C + C_e)V'$$

or

$$C_e = \frac{(V - V')}{V'} C$$

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[1] Van Atta, *Rev. Sci. Inst.*, **1**, 687 (1930).
Rentschler and Henry, *Rev. Sci. Inst.*, **3**, 91 (1932).

[2] Brewer, *Rev. Sci. Inst.*, **1**, 325 (1930).

where $V = V_0 R_1/(R_1 + R_2)$. As V, V', and C are known, C_e may be calculated. If the resistance R is large (10^{10} ohms or greater) it can also be measured by means of C, otherwise a larger condenser must be substituted. The procedure is to open S_4 and close S_3 with S_2 closed and S_1 open, and to time the rate at which the potential difference between the quadrants decreases. As the rate of leakage of charge is proportional to the potential difference, we have

$$\frac{dV}{dt} = -\frac{1}{C + C_e}\frac{dQ}{dt} = -\frac{i}{C + C_e} = -\frac{V}{R(C + C_e)}$$

or

$$\log_e \frac{V}{V^0} = -\frac{t}{R(C + C_e)}$$

where $V = V^0$ when the timing is started, *i.e.*, at $t = 0$. A logarithmic plot of V/V^0 against t yields a straight line of slope $-1/R(C + C_e)$ from which R in electrostatic units may be obtained.

Constant Deflection Method.—This is the most convenient way of using an electrometer when the greatest sensitivity is not necessary. S_3 being open, S_1 is opened with S_2 closed, and the current flowing from the apparatus under investigation passes through R to earth. The potential difference across R is measured by the electrometer and the current is given by V/R. Currents down to about 10^{-13} amp. can be measured in this way without difficulty.

Rate of Deflection Method.—When used in this way the time necessary for the light spot to be deflected through some standard interval is measured with a stop watch as the potential of the quadrants is raised by charges reaching the collecting electrode. This method is more sensitive but it is less convenient and a longer time is required for observations. With S_2 and S_3 open, S_1 is opened and the time of passage, say t, between two standard points on the scale, representing say V_1 and V_2, is recorded. As $C_e(V_2 - V_1) = \Delta Q$, we have

$$i = \frac{\Delta Q}{t} = \frac{C_e(V_2 - V_1)}{t}$$

Currents as small as 10^{-15} amp. may be measured by this method under the most favorable conditions.

Vacuum-tube Amplifiers.—It is possible to measure currents of the order of magnitude of those for which the electrometer is generally employed by the use of a galvanometer and a suitably designed vacuum tube. The principle of the method depends merely on the amplification factor of the ordinary three-electrode tube. A small change in the potential of the grid causes a large change in the plate current. Unfortunately the grid potential *vs.* plate current characteristic is not linear, and calibration over the entire range of use is necessary. To obtain sufficient advantage from such an arrangement it is necessary that the leakage resistance from the grid shall be very large when the tube is in operation. This condition is not fulfilled by most commercial tubes. An especially designed four-electrode tube (FP-54) manufactured by the General Electric Company not only has this characteristic, but also has the further advantage that the voltages necessary for its use are very low so that large-capacity storage batteries may be employed, thus reducing the inevitable voltage fluctuations to a minimum. The chief advantage in the use of these tubes lies in their great ruggedness and portability.

While the current actually measured by the galvanometer is comparatively large, the current flowing to the grid of the tube is small. The same electrostatic shielding and insulation are necessary as in the case of an electrometer. The entire apparatus may be put conveniently in a grounded metal box with a drying agent. The technique of insulation, switches, etc., is identical with that which has been described. In the electrometer tube circuits are the additional complicating factors of batteries, potentiometers, and rheostats. The batteries, with the exception of those merely supplying potential, may be made up of heavy-duty 6-volt storage units which should be kept in good condition. Wherever possible the connections should be soldered, and all sliding contacts should be carefully polished with emery cloth. Battery and emission fluctuations and imperfect contacts are in general the limiting factors on the sensitivity. Recent technical advances for obtaining the highest sensitivity by employing two tubes or operating with a floating grid are described in the current literature.[1]

A very convenient balanced one-tube circuit, which is essentially that suggested by Soller,[2] is shown in Fig. A-7. The proper grid and plate biases are obtained by the iR drop due to the filament current in R_2, R_3, and R_4. Approximate values of these appropriate for the FP-54 tube are given in the figure. The galvanometer, the resistance R_c (which may be included for critical damping), and the cell E are effectively in the position of the galvanometer in a Wheatstone's net. The four arms of this net are: the filament-to-plate resistance of the tube, the filament resistance plus R_2 and R_3, and the resistances R_1, and R_0. The conditions for the balance of this bridge circuit and stability are brought about by choosing correct values for the two resistances R_0 and R_1. For no current to flow through the galvanometer we must have the condition

$$R_0 i_0 - E = R_1 i_1$$

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[1] BREWER, *Rev. Sci. Inst.*, **1**, 325 (1930).
NOTTINGHAM, *J. Franklin Inst.*, **209**, 287 (1930).
DUBRIDGE, *Phys. Rev.*, **37**, 392 (1931).
HULL, *Physics*, **2**, 409 (1932).

[2] SOLLER, *Rev. Sci. Inst.*, **3**, 416 (1932).

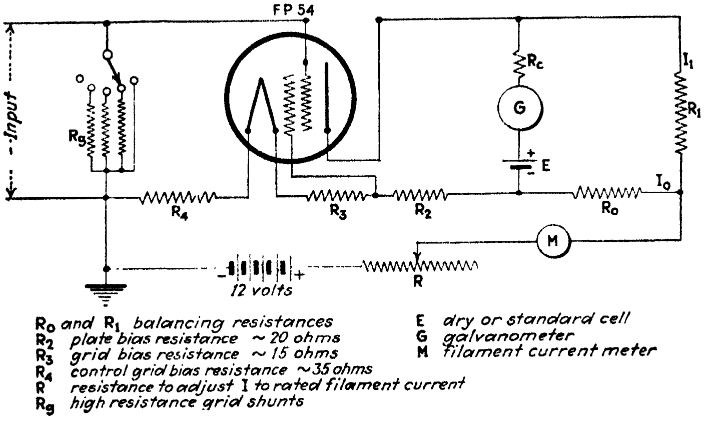
For stable operation a small change Δi_0 in the filament current and the induced change Δi_1 in i_1 must not alter the condition of balance, *i.e.*,

$$R_0(i_0 + \Delta i_0) - E = R_1(i_1 + \Delta i_1)$$

These two equations can be solved for R_0 and R_1, obtaining

$$R_0 = \frac{E}{i_0 - i_1\frac{\Delta i_0}{\Delta i_1}} \qquad R_1 = \frac{E\frac{\Delta i_0}{\Delta i_1}}{i_0 - i_1\frac{\Delta i_0}{\Delta i_1}}$$

As R_0 and R_1 are constant, it is evident from these relations that for proper balancing $\Delta i_0/\Delta i_1$ must be a constant; *i.e.*, the curve of i_1 against i_0 must be a straight line. To obtain the proper values of these resistances, curves of i_1 against i_0 must be obtained under the conditions of operation. In this preliminary adjustment R_1 is removed, and the positions of R_0 and the galvanometer in the circuit are taken by meters capable of reading up to 150 milliamp. and 2 milliamp., respectively. The characteristic curve of i_1 against i_0 is taken. This in general fulfills the condition of linearity in the neighborhood of the rated filament current, and from it the value of i_1 and the slope $\Delta i_1/\Delta i_0$ at this point can be obtained. For a typical tube at $i_0 = 90$ milliamperes, $i_1 = 1$ milliamp., and $\Delta i_1/\Delta i_0 = \frac{1}{50}$; the correct values of R_0 and R_1 for $E = 1.5$ volts are: 37.5 ohms and 1,875 ohms, respectively. The final adjustment is best carried out experimentally by making small variations in R_0 until changes in i_0 give the least galvanometer deflection.



R_0 and R_1 balancing resistances
R_2 plate bias resistance ~ 20 ohms
R_3 grid bias resistance ~ 15 ohms
R_4 control grid bias resistance ~35 ohms
R resistance to adjust I to rated filament current
R_g high resistance grid shunts
E dry or standard cell
G galvanometer
M filament current meter

FIG. A-7.—A simple balanced one-tube amplifying circuit.

After the condition of stable balance has been obtained, the circuit may be calibrated for absolute measurements in the usual way. A potentiometer is connected across the input terminals, and the galvanometer deflection d is plotted in terms of the potential of the control grid e_g.

This graph is then used in the subsequent observations to interpret the observed deflections in terms of the grid potential, which is in turn a measure of the current to the grid i_g through the relation $\Delta e_g = i_g R_g$ (neglecting the current to the grid in the tube). The curve is approximately linear up to a grid potential of 200 or 300 mv. As the resistance of the grid shunt is known, i_g may be obtained. If no grid shunt is in the circuit, the rate of deflection method, as described in connection with the electrometer, may be used for currents down to the order of the grid current in the tube, which is approximately 5×10^{-15} amp.

The following example indicates the dependence of the current amplification factor on the tube characteristics. A change in grid potential Δe_g from the value of e_g, when the galvanometer reads zero, produces a change in plate current of $\Delta i_p = \Delta e_g \partial i_p / \partial e_g$. If the current sensitivity of the galvanometer is k, the galvanometer deflection is given by $d = fk\Delta i_p = fk\Delta e_g g_m$, where f is the fraction of i_p flowing through the galvanometer, and g_m, which is equal to the above derivative $(\partial i_p/\partial e_g)$, is known as the mutual conductance of the tube. Since $\Delta e_g = R_g i_g$, we have

$$\frac{d/i_g}{k} = \frac{fR_g d}{\Delta e_g k} = fR_g g_m$$

The resultant current sensitivity in millimeters per ampere at 1 meter is thus $fg_m R_g$ times the original galvanometer sensitivity. The FP-54 tube has a mutual conductance of about 2.5×10^{-5} amp. per volt, so, if R_g has the value 10^{10} ohms and f is one half, the current amplification factor is 125,000.

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Electrometer Tube:
General Electric pamphlet, G.E.J. 246-A.; G.E.T. 484.

APPENDIX B

VACUUM TECHNIQUE

Fore Pumps.—As all pumps for obtaining high vacua will only work against a small back pressure, of the order of 10 mm. Hg or less, it is necessary to back them with an auxiliary pump capable of maintaining a vacuum of about 1 mm. Hg, which exhausts into the atmosphere. The simplest and most satisfactory of these works on the principle indicated diagrammatically in Fig. B-1. An eccentric cylinder rotates inside a cylindrical cavity with its ends and outer edge in contact with the walls. Leakage past these points is prevented by a film or seal of low-vapor-pressure oil. A strip of metal, *V*, which slides in a slot through the outer case is pressed against the eccentric cylinder by the spring *S*. As the cylinder rotates in the direction of the arrow, the volume of chamber *A* constantly increases and that of chamber *B* decreases during a revolution. This cycle draws gas from the intake and forces it through the spring-valve outlet. Two or more of these units may be arranged in series with the eccentric cylinders on the same shaft. This shaft is driven by a motor at from 200 to 600 r.p.m. These pumps, such as the Cenco Hyvac or Megavac, are capable of producing a vacuum of better than 10^{-3} mm. Hg when new. An increase in the dimensions

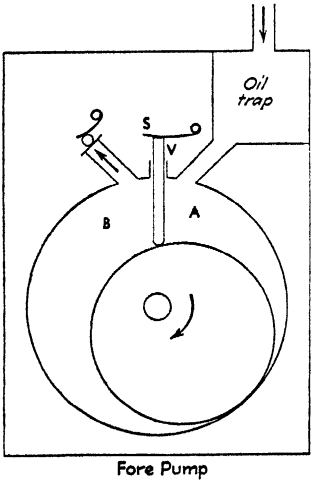

FIG. B-1.—A fore pump.

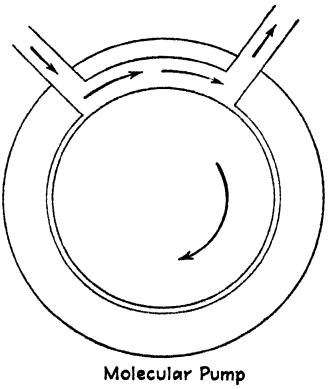

FIG. B-2.—A diagram of a molecular pump.

and speed of rotation, within limits, increases the rate of evacuation. The large pumps have speeds of about 20 liters per minute. For ordinary work where the volumes to be exhausted are not more than a few liters, the small-size pumps with speeds of about 6 liters per minute are adequate.

High-vacuum Pumps.—These pumps are in general of two types. The so-called molecular pump is shown diagrammatically in Fig. B-2. A central cylinder or disk rotates at a very high speed (about 8,000 r.p.m.) with a small clearance, of the order of 0.1 mm., between it and the outer stationary surfaces. The tangential component of velocity given the molecules which strike the rotor forces them from the high-vacuum side toward the fore-pump connection. In the Holweck design the high-vacuum connection is to the central region of a long cylindrical drum, and by means of spiral channels in the stator the molecules are driven to either end of the drum and are removed by the fore pump. These pumps are capable of a high speed and they have the advantage of handling all vapors and requiring no traps for condensation. But because of the high rate of rotation and the small clearances involved they are difficult to make and to keep in condition.

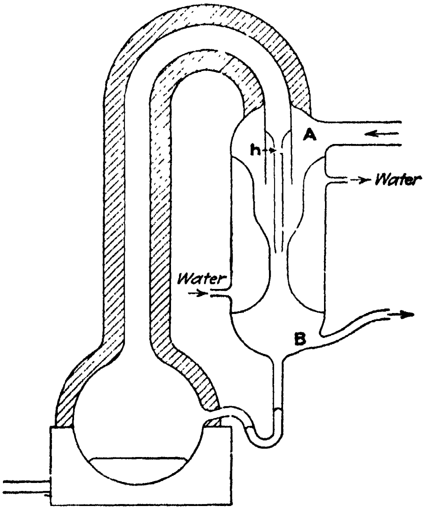

Fig. B-3.—A two-stage water-cooled condensation pump.

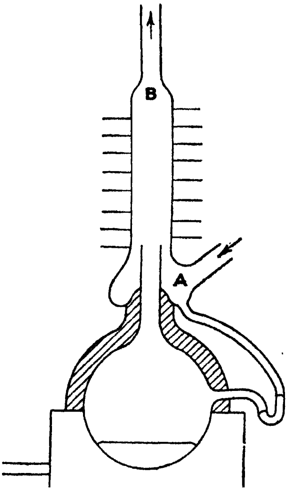

Fig. B-4.—A single-stage air-cooled condensation pump.

The other type of high-vacuum pump in general use is the condensation pump. These require much less care and are easier to operate than the molecular type. Furthermore, when properly designed, they are capable of much higher pumping speeds. As they all involve the evaporation and condensation of some liquid with a comparatively low vapor pressure, such as mercury or various organic oils, some trapping arrangement must be used to keep the vapors from the region being evacuated. These traps will be discussed later.

Figures B-3 and B-4 show two standard designs of these pumps with water and air cooling, respectively. In the pump of Fig. B-4, the liquid is heated by a gas flame or electric heater below the bulb at the bottom of the pump and the vapor streams from the orifice at the top. It condenses on the glass walls of chamber *B*, which for greater efficiency are cooled by radial copper vanes. From there it flows down the walls to chamber *A* and back through the small U-trap into the boiler. Gas present in chamber *A* diffuses into the stream emerging from the boiler and is carried into chamber *B* from which it is removed by the fore pump. Practically no gas diffuses back against the vapor stream from *B* to *A*. Small pumps of this type have speeds of from 1 to 10 liters per second. Figure B-3 represents a two-stage water-cooled pump operating on the same principle. Part of the vapor stream passes through the small holes at *h* and emerges from the large nozzle, while the remainder continues straight down through the smaller nozzle placed just above the constriction. As the clearances are small and the vapor velocity is large at this orifice, the speed is not great but the fore-pump pressure at which it will work is fairly high. The speed of the upper orifice is much greater, and it will work in the vacuum produced by the stage in front of it. Many other designs of these pumps have been suggested, the most rapid being those employing several nozzles in parallel.[1] Such pumps have been built with 19 nozzles and speeds up to 320 liters per second. For the vacuum work described in the text, the simple small-size pumps that are available commercially are quite adequate.

The liquids which have been employed successfully in these pumps are of two types, (1) mercury and (2) low-vapor-pressure organic oils such as Apiezon *A* and *B*,[2] *n*-dibutyl phthalate, *n*-butyl phthalate, butyl benzyl phthalate, dibenzyl phthalate,[3] etc. Mercury has been the standard liquid for many years, and when it is employed successful operation is less sensitive to pump design, boiler temperature, and method of cooling. On the other hand, it has a comparatively high vapor pressure and requires a CO_2 slush or, for the best vacuum work, a liquid-air trap between the pump and the region to be evacuated. The various organic oils, in general, require a better fore vacuum, but they have higher pumping speeds and lower vapor pressures. With these liquids, a trap filled with properly baked-out charcoal is adequate to keep the vapor from reaching the experimental apparatus.[4] This, however, greatly reduces the pumping speed, and a trap surrounded by CO_2 slush is very simple and more efficient. The organic oils at present in use require a more careful maintenance of the optimum working conditions. The correct operating temperature for any particular oil and pump design must be found by trial, but it is in general between 240° and 280°C.

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[1] Ho, *Rev. Sci. Inst.*, **3**, 133 (1932); *Physics*, **2**, 386 (1932).

[2] Burch, *Proc. Roy. Soc.*, **123**, 270 (1929).

[3] Hickman and Sanford, *Rev. Sci. Inst.*, **1**, 140 (1930).

[4] Becker and Jaycox, *Rev. Sci. Inst.*, **2**, 773 (1931).

Vacuum Lines.—While rubber tubing, drying agents, stopcock greases, and waxes may be used in the fore-vacuum region, only substances with very low vapor pressures should be used beyond the high-vacuum pumps, and if possible there should be nothing but glass and metal beyond the vapor traps. The glass connecting tubing on the high-vacuum side of the pumps should be as large in diameter and as short as possible in order to obtain the greatest advantage from a rapid pump. The rate of flow of a gas at a low pressure from a chamber through a tube is given approximately by the following expression

$$F = \frac{Q}{p_2 - p_1} = \frac{9.118 \times 10^3}{W}\sqrt{\frac{T}{M}}\ \text{cm.}^3\ \text{sec.}^{-1}\ \text{at 1 bar}$$

where Q is the amount of gas (in terms of pV) flowing through the tube per second under the influence of the pressure difference $p_2 - p_1$ in bars between the ends; W is a factor analogous to an electrical resistance which depends on the tube dimensions; T is the absolute temperature, and M is the molecular weight of the gas. From this it can be seen that heavy gases flow more slowly than light ones, and that the rate of flow is greater at higher temperatures. The factor W is given by

$$W = \frac{(2.394L + 3.184D)}{D^3}$$

where L and D are the length and diameter of the tube, respectively, in centimeters. The first term is the tube resistance proper and the second the resistance of the orifice admitting to the chamber being evacuated. When the second term is small as it is in the ordinary vacuum system ($L > 10D$), it is seen that F is inversely proportional to L and directly proportional to D^3. Thus it is of the greatest importance to use large-diameter connecting tubing on the high-vacuum side of the pumps. As an example F is 1,000 cc. per second for air at room temperature through a tube 10 cm. long and 1 cm. in diameter, but it is only 10 cc. per second for a tube of the same length 1 mm. in diameter. Traps, cut-offs, and angles decrease the rate of flow and while their effect can be estimated, it cannot be calculated simply. Their use is inevitable, but their number should be reduced to a minimum and they should be of as large tubing as possible.

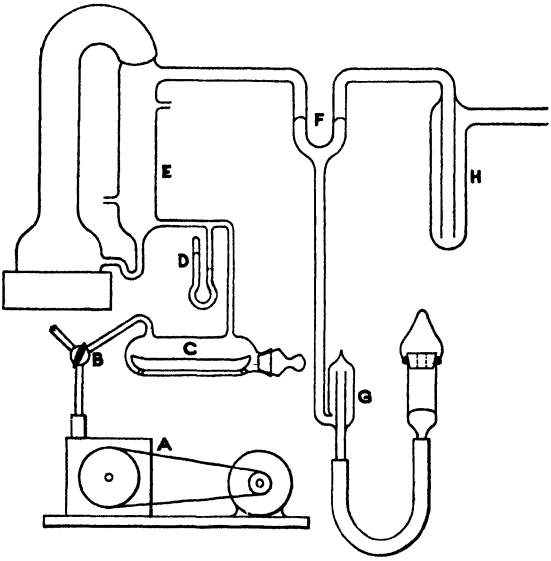
The speed of a pump is defined by the relation

$$S = 2.303\,\frac{V}{t}\,\log_{10}\frac{p_1}{p_2}\ \text{cm.}^3\ \text{sec.}^{-1}$$

where V is the volume in cubic centimeters, which is exhausted from a pressure p_1 to a pressure p_2 in the time t. This means that if a volume V is reduced to $1/e$ of its pressure in t sec. the pump speed is V/t cm.^{3} per second. If the pressure changes by δp, $(p_1 - p_2)$, in a time δt, the log term may be expanded in terms of δp, giving

$$S = \frac{V}{\delta t}\frac{\delta p}{p} = \frac{\delta V}{\delta t}$$

and the speed may be considered as the number of cubic centimeters of gas removed per second at the mean pressure p. When the speed is actually measured, it is necessary, in general, to correct for the resistance of the tube connecting the pump and reservoir. As F and S are of the nature of conductances in series, the true speed S is connected with the apparent speed S' by the relation



A, Fore pump
B, Stopcock for blowing and admitting air to the pump and system
C, P_2O_5 drying chamber
D, Manometer for the fore vacuum
E, Condensation pump
F, Mercury cut-off
G, Air trap
H, Vapor condensation trap

Fig. B-5.—A simple vacuum system.

$$\frac{1}{S'} = \frac{1}{S} + \frac{1}{F}$$

It is frequently a convenience to be able to disconnect the pumps from the experimental apparatus. A large-bore stopcock may be used for this purpose or a mercury cut-off, as shown at F in Fig. B-5. An alternative design is to have the cut-off similar in construction to the vapor trap *H*, but with a narrow tube, through which the mercury is raised, connected to the bottom of the bulb. The distance from *F* to the trap *G* (which fulfills the purpose of catching any air bubbles that may get into the mercury) should be slightly greater than the barometric height. In this arrangement there is always a positive outward pressure at the waxed junctions between the glass and heavy-walled rubber tubing leading to the mercury reservoir. This commercial rubber tubing, when intended for use in any part of a vacuum system, should be boiled in caustic soda, washed in distilled water, and thoroughly dried before use. It should not be heated directly when waxing. The glass is warmed and the wax applied to it. The rubber tubing is then slipped over the end and the joint completed with a waxing iron.

The trap for the removal of condensable vapors is generally made with a reentrant seal as shown at *H* of Fig. B-5. A Dewar flask, containing the freezing liquid or slush, supported by a clamp surrounds the trap. For the removal of mercury vapor or the vapors of the oils used in condensation pumps, a slush of CO_2 (commercial "dry ice") in acetone, alcohol, or ether is quite satisfactory. Mercury is removed more rapidly and completely if liquid air is used. For the removal of water vapor, liquid air is necessary; but if an efficient drying chamber is included in the vacuum line and care is used in admitting air and in blowing, there should be very little water vapor present. When oil is used in the pumps, and the apparatus contains no mercury cut-offs or McLeod gauges, the trap may be filled with coconut charcoal kept in place with metal gauze wadding, and no refrigerant need be used.

Vacuum Gauges.—Pressures in vacuum work are generally measured in one of the following three units: (1) millimeters of mercury, mm. Hg; (2) microns μ, (thousandths of a millimeter of mercury); (3) bars[1] (dynes per square centimeter). Taking the acceleration of gravity as 980.6 cm. sec.$^{-2}$ and the density of mercury as 13.55 grams per cubic centimeter, we have the following relation between these three units:

$$1 \text{ mm. Hg} = 10^3\mu = 1{,}325 \text{ bars}$$

As the atmospheric pressure is about 1.0132×10^6 dynes per square centimeter, a bar is approximately one-millionth of an atmosphere. The unit in most general use is probably the millimeter of mercury because of the extensive use of this element in barometers and U-tube manometers. The latter are the most convenient pressure-measuring devices down to a few millimeters of mercury. They may be constructed very simply from a U-tube of the desired length with one end sealed off. They should be baked and filled with mercury under vacuum. For the measurement of lower pressures, other more sensitive types of manometer must be used Many different principles and forms have been suggested which are fully discussed in the literature. We shall consider here only four of the simplest of these which are in general use.

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[1] The meteorological unit called the bar is 10^6 times the unit of the same name used in vacuum work. This latter quantity is sometimes known as the barye or microbar.

McLeod Gauge.—In the McLeod gauge, the top of which is shown in Fig. B-6, mercury is raised from a reservoir, which in the simplest form is similar to the mercury cut-off arrangement of Fig. B-5, and, when the level reaches the point a, the gas in the bulb b is cut from the system. As the mercury rises further, the gas is compressed into the capillary at the top of the bulb. This decrease in volume and consequent increase in pressure, in accordance with the relation $pV = RT$, provides the amplification factor upon which the operation of the gauge is based. As the action of the gauge depends on the gas law, it is obvious that the gauge will not measure condensable vapors but only pressures due to permanent gases. There are two general methods of use: (1) The mercury level in the side capillary (of the same bore as the capillary on the top of chamber b in order to equalize the surface-tension forces in the two tubes) is raised to the level of the sealed end of the other capillary and the difference in the mercury levels, h, in the two tubes is recorded. (2) The mercury is raised to some fiducial mark in the capillary above b, say a distance q from the top, and the difference in the levels, h', in the two tubes noted. If V is the volume of the bulb, and l and A are the length and cross-sectional area of the sealed capillary, respectively, the pressure in the system using method 1 is given by

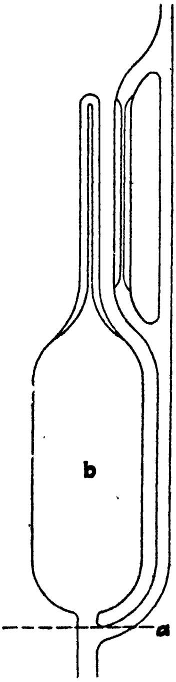

FIG. B-6.—A McLeod gauge.

$$p(V + lA) = h(hA)$$

or

$$p = \frac{A}{V + lA}h^2 \cong \frac{A}{V}h^2 \text{ mm. Hg}$$

where all dimensions are measured in millimeters. Thus p is proportional to h^2 and a set of parabolas plotted on cross-section paper and supported behind the capillaries permits the direct reading of pressures.

In method 2,

$$p(V + lA) = h'(qA)$$

or

$$p = \frac{qA}{V + lA}h' \cong \frac{qA}{V}h' \text{ mm. Hg}$$

and hence a linear scale may be placed along the side capillary for the direct reading of pressures. These gauges may be used down to about

10^{-5} mm. Hg, but as has been mentioned previously they indicate only the presence of permanent gases. The volume V should not be greater than a few hundred cubic centimeters or the readings will take inconveniently long, and the capillaries should not be less than 0.5 mm. in diameter or even the cleanest mercury will tend to stick. The average capillary diameter can best be found by filling a known length with mercury which is subsequently weighed [A = mass/(density × length)]. The volume of the bulb after assembly may be found in the same way. The sealed end of the capillary above b should be as flat as possible to permit accurate measurements with the mercury near the top. The gauge and tube leading up to it should be baked or thoroughly torched under vacuum before the mercury is admitted.

Quartz Fiber Gauge.—This simple type of gauge was suggested by Langmuir[1] and further investigated by Haber and Kerschbaum.[2] It consists merely of a fine quartz fiber about 0.005 cm. in diameter and 5 or 10 cm. long, suspended down the center of a glass tube 1 or 2 cm. in diameter. The fiber is introduced into the tube which has one end sealed as in a test tube, and the bottom, where the fiber rests, is heated in a blow torch until it softens. When the fiber has stuck, the tube is quickly inverted and the fiber hangs down the center. It makes a very convenient gauge for small spaces or for apparatus which is sealed from the pumps. It is, of course, baked or torched under vacuum in the usual manner. When ready for use the tube is gently tapped or the fiber set in vibration by some other means,[3] and the end is observed perpendicular to the plane of vibration by means of a low-powered microscope with an eyepiece scale. The time t necessary for the amplitude to decrease to half its original value is noted. It has been shown by Haber that this time is related to the pressure p and the molecular weight M of the gas by the relation

$$p\sqrt{M} = \frac{b}{t} - a$$

where b and a are constants of the fiber. Thus the gauge must be calibrated against a McLeod at two pressures, using a known gas in order to determine the constants a and b. This type of gauge covers roughly the same pressure range as a McLeod. It will measure vapor pressures, but it is necessary to know the type of gas or vapor present for accurate work.

Resistance Manometer.—In this form of gauge, whose development has been due largely to Pirani and Hale,[4] a wire is heated by an electric current and its resistance, which is a function of the temperature and hence of the gas pressure, is measured. As the pressure is determined from the cooling effect of the gas on the wire, and as this is different for different gases, the type of gas present must be known. To a first approximation, however, the differences in the cooling effect per molecule present for all gases with the exception of hydrogen are small, and for ordinary work the gauge need be calibrated for air and for hydrogen only. The wire is strung under tension from a support in a bulb capable of being immersed in a constant-temperature bath. A fine wire with a large temperature coefficient of resistance is most satisfactory. The substances in general use are platinum or tungsten; a wire from 0.03 to 0.06 mm. in diameter and 10 or 20 cm. long will cover a convenient pressure range. This may be bent in the form of a hairpin and kept taut by a small spiral spring made from 5-mil tungsten wire wound on a No. 45 drill. The operating temperature of the wire is not very high; about 100°C. has been found satisfactory. The wire temperature may be found from its resistance at low current densities and the temperature coefficient. Ordinary tungsten-filament lamps (20 to 40 watt) may be used, but they are not suitable for a low pressure range. The pressure range of a properly constructed gauge is about the same as that of a McLeod. The filament can be put into one arm of a Wheatstone's bridge, the three other resistances having negligible temperature coefficients, and the bridge arranged to balance with the wire at about 100°C. If the voltage applied to the bridge at balance for a pressure p in the bulb is V and that for a pressure 0 is V_0, it is found that

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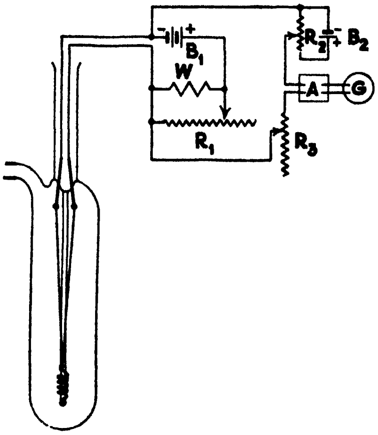
[1] LANGMUIR, *J. Am. Chem. Soc.*, **35**, 107 (1913).

[2] HABER and KERSCHBAUM, *Zeits. Elektrochem.*, **20**, 296 (1914).

[3] BECKMAN, *J. Optical Soc. Am.*, **16**, 276 (1928).

[4] HALE, *Trans. Am. Electrochem. Soc.*, **20**, 243 (1911).



W, Small resistance with a low temperature coefficient.
R_1, R_2, R_3, Adjusting resistances.
B_1, Main battery (4 volts)
B_2, Balancing battery
A, Galvanometer shunt.

FIG. B-7.—A resistance vacuum gauge (Pirani gauge).

$$\frac{V^2 - V_0^2}{V_0^2} = kf(p)$$

where $f(p) \cong p$ below about 0.1 mm. Hg. The constant k for air or hydrogen is determined by calibration against a McLeod. A continuously reading arrangement suggested by Skellett[1] is shown in Fig. B-7. The battery B_1 in series with the filament and a fixed resistance W, having a negligible temperature coefficient, heats the filament to the proper temperature and variations in the potential drop across it induced by changes in the pressure are recorded by the galvanometer. The current through the galvanometer at the lowest obtainable pressure is balanced out by the auxiliary battery B_2 and the adjusting resistances R_1 and R_2. R_3 is a protective resistance which together with the Ayrton shunt determines the sensitivity. The galvanometer deflection is proportional to the pressure over a wide range.

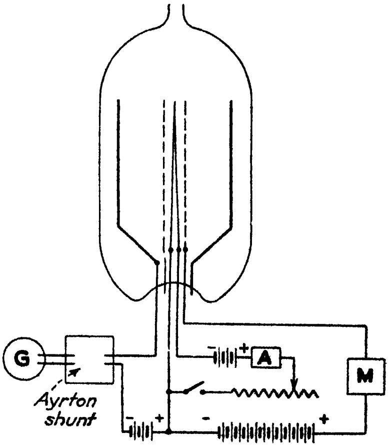


FIG. B-8.—An ionization gauge.

Ionization Gauge.—This type of gauge, suggested by Buckley,[2] is very similar to the ordinary three-electrode vacuum tube. An electron current from the filament to the grid ionizes some of the gas atoms or molecules present, and this positive ion current flows to the plate and is detected by a galvanometer. While a radio tube can be used, it is not so satisfactory as a properly designed gauge in which the spacing between the grid and plate is large. Such gauges may be obtained commercially from the Western Electric Company, or they may be constructed in the laboratory. A tungsten filament is surrounded by a spiral tungsten grid 1 or 2 mm. away and this system is placed coaxially inside a cylindrical plate about 2 cm. in diameter. The entire system may be mounted on one press or the plate may be supported by a separate seal. The bulb is baked out and the elements freed from gas in the usual manner. The electrical connections are shown in Fig. B-8. The filament-heating circuit is of the usual form; a potential of +100 or 200 volts is applied to the grid and about −20 volts to the plate. Thus no electrons reach the plate, but positive ions formed outside the grid are drawn to it and recorded by the galvanometer. The sensitivity of the gauge depends on the potentials employed and on the electron current to the grid. This is measured by the meter M, and it is maintained at some convenient value between 5 and 25 milliamp. This gauge is capable of recording lower pressures than the other gauges which have been described; pressures as low as 4×10^{-8} mm. Hg have been measured accurately. The galvanometer deflection is proportional to the pressure below about 3×10^{-4} mm. Hg for an electron current of 25 milliamp. and below about 10^{-3} mm. Hg for an electron current of 5 milliamp. As the free path and the probability of ionization depend on the particular gas, the gauge must be calibrated against a McLeod for each gas that is to be used. For this reason the ionization gauge has not the wide range of convenient application of the other gauges.

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[1] SKELLETT, *J. Optical Soc. Am.*, **15**, 56 (1927).

[2] BUCKLEY, *Proc. Nat. Acad. Sci.*, **2**, 683 (1916).

Gas Systems.—It is frequently necessary to fill an experimental tube with gas at some specified pressure or to let gas leak slowly into a tube under controlled conditions. A system designed to fulfill these requirements is shown in Fig. B-9. As with the vacuum system itself, it is most conveniently supported by a welded-iron framework with crossbars 12 or 18 in. apart and uprights at the necessary intervals for rigidity. This is mounted in a vertical plane by angle irons screwed to a table top. The glass apparatus may be supported at intervals with clamps using asbestos tape packing. Mercury reservoirs should be held by heavy ring clamps around their bases. The tubing may alternatively be attached to the frame by wrapping it with a layer of asbestos tape and then a layer of solder-covered copper wire; this latter may then be soldered directly to the frame. For this system the tubing and stopcocks need not be large, as the pressures used are generally of the order of several centimeters of mercury.

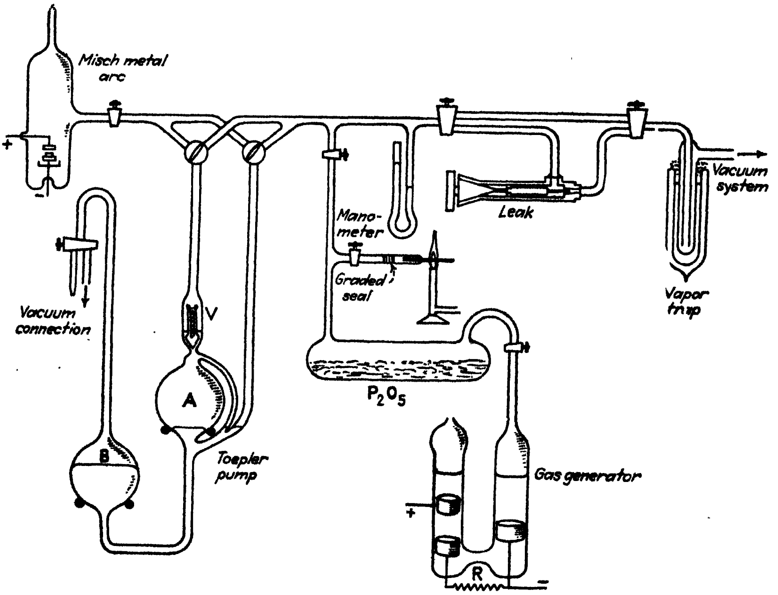

FIG. B-9.—The details of a representative gas system.

The principal part of the gas system is the Toepler pump which is composed of the chambers *A* and *B* and the valve *V*. The by-pass around chamber *A* is to prevent violent mercury surges when working at large pressure differences. Chamber *B* and the air and vacuum connections to it may be replaced by a rubber tubing and hand-operated reservoir system, as shown in Fig. B-5 for the mercury cut-off. As the mercury level is raised in chamber *A*, the gas is forced up through the valve *V*. This is of glass, ground into a seat, and contains a piece of iron rod sealed inside it to increase its weight. After the mercury level has been raised past this valve, the level is lowered and the valve seats itself in a mercury seal, trapping the gas above it. The level is lowered further, until gas flows into the chamber again from the connections at the bottom. With the three-way stopcocks at the top properly set, the pump circulates gas in a clockwise direction. These stopcocks can be set so that gas is pumped from the storage tanks into the vacuum system, or by reversing the cocks it can be pumped in the opposite direction. The pump may be removed from the system altogether by setting the stopcocks to connect the storage tanks directly to the vacuum system.

The gases most frequently required are helium, neon, hydrogen, oxygen, and nitrogen. A method for the production and purification of the last has been described in Chap. VIII. Oxygen and hydrogen may be prepared electrolytically from a solution of NaOH using the gas generator shown in Fig. B-9; the indicated polarity is for the collection of hydrogen. The central electrode, which is connected to the negative electrode through the high resistance *R* (about 10,000 ohms) evolves a small amount of gas and prevents oxygen from being drawn over into the chamber leading to the vacuum system when hydrogen is being generated rapidly. The chamber should be flushed out several times before the hydrogen intended for use is admitted into the P_2O_5 drying bulb. Hydrogen may also be admitted to the system up to its partial pressure in a Bunsen flame through a palladium tube, as shown in the diagram. This tube, which is closed at its outer end, is sealed through a soft glass tube which is in turn connected by a graded seal to the hard glass system. The hydrogen admitted in this way is very pure and may be used directly. Higher pressures may be obtained by pumping it off from time to time into a storage tank as it accumulates. Helium and neon may be purchased fairly pure in tanks and the final purification accomplished with a coconut-charcoal trap. This is connected to the vacuum system and baked out for several hours at as high a temperature as the glass will stand. It is then immersed in liquid air and the rare gas circulated through it by means of the Toepler pump. (The connections for this circulation are not shown in the diagram.) Alternatively these gases may be stored in a container having two heavy electrodes one of which supports a piece of misch metal (rare-earth alloy). A heavy arc, run to the misch metal as a cathode, vaporizes this metal which absorbs practically all the foreign gases that may be present.

The purified gases may be admitted directly to the vacuum system, or as in the case of the e/M apparatus they must be admitted slowly through an artificial leak. A desired pressure difference may thus be obtained using a differential pumping method. Various forms of these artificial leaks are in use. The simplest consists of a very finely drawn capillary tube sealed internally in the gas line. With this type of leak the rate of flow is controlled entirely by the back pressure. If the rate of leak is too slow at the highest back pressures that can be obtained, it may be increased by blowing a hole in the side of the outer tube, snipping off a small section of the capillary with tweezers and resealing the hole. A mechanical valve whose rate of leak is adjustable may be made as indicated in Fig. B-9. A threaded steel rod with a finely tapered point is screwed into a seat by means of the knurled head on a steel cone whose point is extended to key into the other end of the threaded rod. This steel cone is ground into a brass cone of the same taper and the joint made vacuum tight with stopcock grease. Other artificial leak designs may be found in the literature.[1]

General Technique. *Greases, Waxes, and Cements.*—These are to be avoided as much as possible in all vacuum work, particularly where the highest degree of evacuation is desired. Vapor traps should be placed in the vacuum line between all stopcocks or greased joints and the experimental apparatus, whenever this can be done. Unfortunately, for large pieces of apparatus, in particular those involving metal construction, it is not always possible to dispense with these waxes. When parts of an apparatus must be constructed of metal, it is always advisable to use rolled sheets or tubes rather than castings as the latter are more subject to leaks. When castings are necessary, the surfaces should be thoroughly tinned inside and out.

Greases are necessary at stopcocks and occasionally on rubber gaskets in connection with metal apparatus, but they are seldom satisfactory for pressures lower than 10^{-3} or 10^{-4} mm. Hg. Greases, such as Lubriseal and Apiezon, have vapor pressures of this order of magnitude, and when frequent motion of the parts is necessary, as in a stopcock, the grease is gradually squeezed out and small leaks develop through the stopcock or from the atmosphere. Waxes of various consistencies which are satisfactory for rough vacuum work may be made from white beeswax and rosin. A convenient mixture is half beeswax and half rosin; a harder wax may be made using 9 parts of rosin to 1 of beeswax. The ingredients should be as pure as possible and, after melting them together, the wax may be cast in sticks about 1 cm. in diameter for convenience in application. Ordinary sealing wax may also be used although it is not quite so easy to apply.

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[1] HOPFIELD, *J. Optical Soc. Am.*, **12**, 391 (1926).
PETERS and KLEIN, *J. Optical Soc. Am.*, **15**, 59 (1927).

When waxes are necessary for higher vacuum work only those with very low vapor pressures should be chosen. Certain grades of sealing wax are satisfactory, and there are a number of other waxes designed for vacuum work such as DeKhotinsky, Picein, Everett, etc., which are commercially available. The vapor pressures of these various waxes are not well known, but they can be used satisfactorily for intermediate vacuum work. In applying any waxes, the metal or glass parts should be heated separately above the melting point of the wax and thoroughly dried before the wax is applied. The parts may then be put together and the final joint made with more wax and a hot iron.

In addition to these waxes there are certain cements and lacquers made from organic compounds with low vapor pressures. The use of glycol phthalic anhydride has been described by Sager and Kennedy.[1] Apiezon sealing compound and Duco cement are frequently useful, and the line of glyptal lacquers is particularly valuable for stopping leaks and making metal-to-glass joints because of their low vapor pressures and heat resistant properties.

Mercury Cleaning.—The mercury used in pumps, gauges, cut-offs, etc., should be as pure and clean as possible. The preliminary cleaning can be done by bubbling dry air through it for several hours. The scum may be removed by passing it through filter paper pierced with a few needle holes and supported in a funnel. It is then put into the container *A* of the vacuum still shown in Fig. B-10. A rough vacuum system is connected to the still and the mercury raised into the boiler. Clean mercury is drawn up in the other arm to within a few inches of the vacuum connection. The mercury is heated by an electric heater or gas ring and distilled over and collected in the container *B*. Any lead which may be present is left behind in the still and highly volatile impurities are drawn off by the pump.

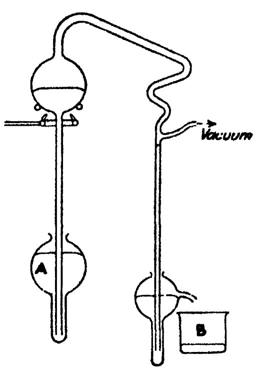

FIG. B-10.—A mercury still.

Preparation of Experimental Tubes.—Electrode construction from nickel, molybdenum, or tungsten is a simple mechanical process, but all joints should be made by welding. Small pieces may be arc welded, in the cone of a Bunsen flame to prevent oxidation, by simply striking a direct-current arc to the desired spot with a sharpened carbon electrode connected to the positive pole of the battery or generator. A protective series resistance capable of carrying the necessary current should, of course, be included in the circuit. Better results may be obtained by welding in an atmosphere of hydrogen under a bell jar. For small joints between wires or sheets of these metals, spot-welding is the most convenient method. A small current transformer with a controlling resistance in the primary and a secondary capacity of about 100 amp. may be used satisfactorily. The secondary, which is made of two or three turns of copper strip, is connected by heavy flexible leads to two copper bar electrodes held in chucks which can be clamped firmly together with a foot lever. A foot switch in the primary of the transformer enables the circuit to be closed while the parts to be welded are held in place and pressed tightly together by the copper electrodes. The weld is frequently improved if a little alcohol is used as a flux. The value of the primary current is adjusted with the rheostat to suit the size of the pieces to be welded; one or two surges are generally sufficient.

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[1] SAGER and KENNEDY, *Physics*, **1**, 352 (1931).

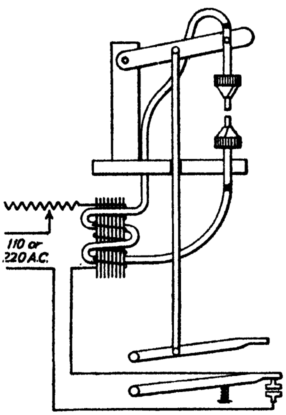

Fig. B-11.—A spot-welding apparatus.

The technique of tube construction, metal-to-glass seals, etc., is fully described in treatises on glass blowing and working. After the individual parts of a system or an experimental tube have been constructed, they should be carefully tested for leaks before being finally mounted in place for permanent evacuation. Such leak testing in glass may be done by attaching the apparatus to a fore pump and going over it, the joints in particular, with the high-tension terminal of a small therapeutic Tesla coil. An ordinary small induction coil may be used, in which case one terminal is connected to the metal pump and the other is held in a heavy rubber tube or waxed to the end of an insulating rod. When the terminal is near a pinhole or crack in the glass walls, an intense thread of discharge will jump to the fault which may be discerned easily against the general glow-discharge background. The point may be marked with a wax pencil and worked over in a flame after air has been admitted. Leaks in the metal parts of a vacuum system are more difficult to discover. A discharge may be maintained in a rough vacuum and its color noted as a cotton wad saturated with ether is applied to likely places. If there is a hole the ether will impart a characteristic white or bluish color to the discharge, and the leak may be stopped with wax or cement.

If the apparatus is to be sealed from the pumps, a constriction should be made in the glass evacuating tube by thickening it in a flame. The tube is then exhausted and baked in an oven for several hours at about 450°C., or at as high a temperature as the glass will stand safely. Baking ovens may be made of asbestos board fastened together with angle irons, with festoons of chromel or nichrome heating wire on the inside. Large ovens are quite heavy and may be lowered over the tube by a system of pulleys and counterweights if necessary. The pumping connection is brought up through a hole in the asbestos board forming the floor of the oven. Small light ovens, which have been used satisfactorily, can be made very simply from hemicylindrical steam-pipe insulating units. The two halves are clamped together with brass strip and small spirals of heating wire are strung inside parallel to the axis. The temperature may be measured with a thermometer or thermocouple and it should be carefully controlled so that the glass does not soften. After the main part of the baking process is completed, which in general takes from 2 to 4 hr. depending on the size and construction of the apparatus, the metal elements in a tube should be heated separately to a higher temperature. If the tube contains a filament, it may be lighted and an electron current drawn to the other electrodes. This current heats these elements by electron bombardment and they should be raised to a considerably higher temperature than they will ever reach when in use. If an induction furnace is available, the elements may be heated by it up to a cherry red and maintained in that temperature range for several minutes at a time. The baking and heating processes should be continued till there is no readable pressure on the vacuum gauge with the elements at these temperatures. The constriction is then torched till the glass nearly softens. It is maintained at this temperature for several minutes and then completely softened over as short a length as possible and rapidly sealed off.

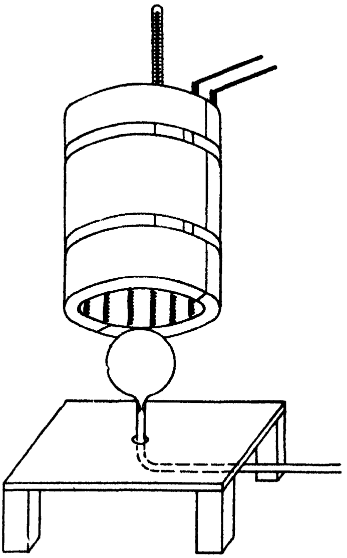

FIG. B-12.—A baking furnace.

Evaporation and Sputtering.—It is frequently of use to be able to deposit a permanent thin film of metal upon an insulator, as in the manufacture of conducting quartz-fiber suspensions, mirrors, thin metallic films for electron and X-ray diffraction, etc. An apparatus designed for evaporating metals, alloys, or quartz from a tungsten filament or from a graphite crucible has been described by Cartwright and Strong.[1] The films prepared in this way are frequently more homogeneous and permanent than those obtained by sputtering. For the details of the apparatus and technique, reference should be made to that article.

---

[1] CARTWRIGHT and STRONG, *Rev. Sci. Inst.*, **2**, 189 (1931).

For the preparation of electrometer fibers and the mirrors and thin films described in the text the simple sputtering apparatus shown in Fig. B-13 is adequate. A flat brass or iron plate has a hole drilled in it for a vacuum connection and is supported on a low stand for convenience. A bell jar with a ground joint at the top is fitted with a single-hole rubber stopper through which passes a glass tube a few millimeters in internal diameter. A copper wire with a hook on the end is inserted in this tube and engaged in the hook of a wire which is welded to the center of the sheet of material from which sputtering is to take place. The latter is then drawn up flat against the end of the glass tube and the copper wire waxed in place at the top. This sheet of metal from which the sputtering is to take place should be large enough to cover the object to be sputtered in order to obtain a uniform coat. The object should be baked for several hours at about 200°C. to free its surface completely from water and other vapors in order to insure a uniform and permanent coat. It may be supported on a piece of large-diameter glass tubing a few centimeters below the metal plate. The bell-jar joints are then made tight by running soft wax round them with an iron.

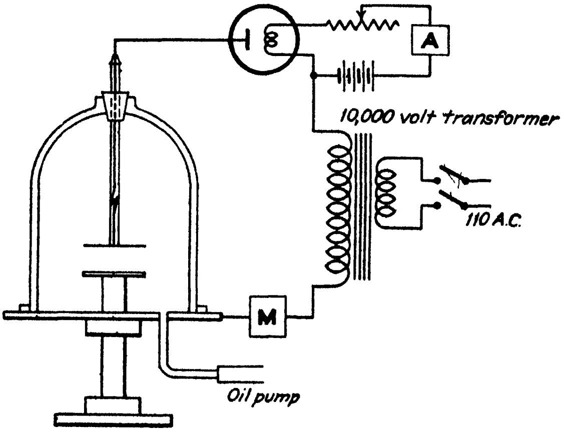

FIG. B-13.—A sputtering apparatus.

A small 10,000-volt transformer is connected in series with the base plate, a kenotron, and the sputtering terminal in such a way that the latter is the cathode. The oil pump is then started, and when its limit is reached at about 10^{-2} mm. Hg the transformer switch is closed. The discharge is likely to be unstable for a few minutes, but when the equilibrium conditions are established the dark space of the discharge should extend about 1 cm. from the cathode. The conditions are not particularly critical, and the growth of the sputtered layer on the lower surface can be watched by means of a light suitably placed behind the apparatus. The time required will depend on the material being sputtered, the thickness of the coat desired, the gas pressure, and the current density. The mechanism of the sputtering process is not well understood,[1] and in general the best procedure is to inspect the surface from time to time and stop the process when the desired coat has been produced. Under ordinary conditions silver, gold, platinum, and copper sputter rapidly, while nickel, molybdenum, tungsten, and aluminium are deposited more slowly. With a good fore pump, and the conditions as outlined above, a satisfactory mirror coat of platinum or gold can be obtained in from 40 to 60 min. Half- and quarter-coated surfaces take proportionately shorter times.

General References

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[1] COMPTON and LANGMUIR, *Rev. Mod. Phys.*, **2,** 186 (1930).

FUNDAMENTAL PHYSICAL CONSTANTS[1]

Velocity of light	c	$= (2.99796 \pm 0.00004) \times 10^{10}$ cm. sec.$^{-1}$
Volume of perfect gas (0°C., A_{45})	R	$= 22.4146 \pm 0.0008$ liter mole^{-1}
Ice point (absolute scale)	T_0	$= 273.18 \pm 0.03°$ Absolute.
Mechanical equivalent of heat	J_{15}	$= 4.1852 \pm 0.0006$ abs.-joule cal.$_{15}{}^{-1}$
Faraday	F	$= 9648.9 \pm 0.7$ abs.-e.m.u. gram-equiv.$^{-1}$
Electronic charge	e	$= (4.770 \pm 0.005) \times 10^{-10}$ abs.-e.s.u.
	e/c	$= (1.5911 \pm 0.0016) \times 10^{-20}$ abs.-e.m.u.
Specific electronic charge	e/m	$= (1.761 \pm 0.001) \times 10^{7}$ abs.-e.m.u. gram^{-1}
	$(e/m)c$	$= (5.279 \pm 0.003) \times 10^{17}$ abs.-e.s.u. gram^{-1}
Planck constant	h	$= (6.547 \pm 0.008) \times 10^{-27}$ erg. sec.
Rydberg constant (hydrogen)	R_H	$= 109{,}677.759 \pm 0.05$ cm.$^{-1}$
Rydberg constant (infinite mass)	R_∞	$= 109{,}737.42 \pm 0.06$ cm.$^{-1}$
True grating space of calcite (20°C.)	d'_{20}	$= (3.0283 \pm 0.0010) \times 10^{-8}$ cm.
Avogadro's number	$N_0 = Fc/e$	$= (6.064 \pm 0.006) \times 10^{23}$ mole^{-1}
Gas constant per mole	R_0	$= (8.3136 \pm 0.0010) \times 10^{7}$ erg. deg.$^{-1}$ mole^{-1}
Boltzmann constant	$k = R_0/N_0$	$= (1.3709 \pm 0.0014) \times 10^{-16}$ erg. deg.$^{-1}$
Second radiation constant (exp. value)	c_2	$= 1.432 \pm 0.003$ cm. deg.
Stefan-Boltzmann constant (exp. value)	σ	$= (5.735 \pm 0.011) \times 10^{-5}$ erg. cm.$^{-2}$ deg.$^{-4}$ sec.$^{-1}$
Wien displacement constant	$A = c_2/4.9651$	$= 0.28836 \pm 0.00011$ cm. deg.
Mass of electron	$m_0 = \dfrac{e}{c(e/m)}$	$= (9.035 \pm 0.010) \times 10^{-28}$ gram
Mass of hydrogen atom	M_H	$= (1.6618 \pm 0.0017) \times 10^{-24}$ gram
Mass of α particle	M_α	$= (6.598 \pm 0.007) \times 10^{-24}$ gram
Specific charge of α particle	$2e/M_\alpha$	$= 4823.1 \pm 0.6$ abs.-e.m.u. gram^{-1}
Ratio, mass H atom to mass electron	M_H/m	$= 1839 \pm 1$
Wave number associated with 1 abs.-volt	$\bar{\nu}_0 = \bar{\nu}/V''$	$= 8{,}106 \pm 3$ cm.$^{-1}$ abs.-volt^{-1}
Wave length associated with 1 abs.-volt	$\lambda_0 = \lambda V''$	$= (12{,}336 \pm 5) \times 10^{-8}$ cm. abs.-volt
Zeeman displacement per gauss	$\Delta\nu/H = \dfrac{(e/m)}{4\pi c}$	$= (4.674 \pm 0.003) \times 10^{-5}$ cm.$^{-1}$ gauss^{-1}

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[1] BIRGE, *Phys. Rev. Suppl*, **1,** 1 (1929).

PERIODIC TABLE AND NORMAL ELECTRON STRUCTURES OF THE ELEMENTS

(O = 16)

Arrangement by Dr G. H. Shortley

	s electrons		*p* electrons							*d* electrons									
	1	2	1	2	3	4	5	6		1	2	3	4	5	6	7	8	9	10
1*s*	1 H 1.00778	2 He 4 00216																	
2*s*	3 Li 6 928	4 Be 9 02																	
2*p*			5 B 10 806	6 C 12 0036	7 N 14 008	8 O 16.0000	9 F 9 0000	10 Ne 20.18											
3*s*	11 Na 23.000	12 Mg 24.30																	
3*p*			13 Al 26 97	14 Si 28 08	15 P 30 9825	16 S 32 065	17 Cl 35 457	18 A 39 94											
4*s* 3*d*	19 K 39 105	20 Ca 40 09							(0 4*s*)										
									3*d*: (1 4*s*)					24 Cr 52.011					29 Cu 63 55
									(2 4*s*)	21 Sc 44 96	22 Ti 47 90	23 V 50.95		25 Mn 54 95	26 Fe 55 84	27 Co 58.95	28 Ni 58 69		30 Zn 65 38
4*p*			31 Ga 69.72	32 Ge 72 65	33 As 74 934	34 Se 78 96	35 Br 79 916	36 Kr 83 77											
5*s* 4*d*	37 Rb 85 43	38 Sr 87 54							(0 5*s*)										46 Pd 106.7
									4*d*: (1 5*s*)				41 Cb 92.90	42 Mo 95 97	43 Ma	44 Ru 101 65	45 Rh 102 9		47 Ag 107 880
									(2 5*s*)	39 Y 88 93	40 Zr 91.2								48 Cd 112 40
5*p*			49 In 114.8	50 Sn 118.72	51 Sb 121.79	52 Te 128 03	53 I 126 932	54 Xe 131.27											
6*s* 5*d* 4*f*	55 Cs 132 917	56 Ba 137 43							(0 6*s*)									77 Ir 193 04	
									5*d*: (1 6*s*)									78 Pt 195 2	79 Au 197 21
									(2 6*s*)	57* La 138 90	72 Hf 178 6	73 Ta 180 89	74 W 183 96	75 Re 186 22	76 Os 190 31				80 Hg 200 62
6*p*			81 Tl 204 41	82 Pb 207 22	83 Bi 209 00	84 Po 210.	85	86 Rn 222.											
7*s* 6*d*	87	88 Ra 225 97							6*d*: (2 7*s*)	89 Ac 227	90 Th 232 12	91 Pa 231	92 U 238.18						

*Rare earths 4 *f* electrons

1	2	3	4	5	6	7	8	9	10	11	12	13	14
58 Ce 140.2	59 Pr 140 9	60 Nd 144.25	61 Il	62 Sa 150.43	63 Eu 152.0	64 Gd 157.0	65 Tb 159.2	66 Ds 162.46	67 Ho 163.5	68 Er 167 6	69 Tu 169.4	70 Yb 173.0	71 Lu 175 0

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